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PROCEEDINGS OF THE SOCIETY OF ARTS

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PROCEEDINGS OF THE SOCIETY OF ARTS

FORTY-FOURTH YEAR, 1905-1906

BOSTON, May 10, 1906.

THE 624th regular meeting and the 45th annual meeting of the SOCIETY OF ARTS was held at the Institute, Room 22, Walker Building, on Thursday evening, May 10, 1906, at eight o'clock. Professor Gaetano Lanza presided. One hundred and thirty persons were present.

The election of an Executive Committee for the ensuing year was the first item of business. The nominations sent in by the Nominating Committee were as follows: Mr. George W. Blodgett, chairman, Colonel E. H. Hewins, Mr. James P. Munroe, Professor James F. Norris, Mr. Grosvenor T. Blood. The Secretary was empowered to cast one ballot for these gentlemen. For Secretary, the name of Professor Walter S. Leland was presented, and he was elected for the ensuing year.

The chairman then presented Mr. Herbert O. Keay, who read an interesting and instructive paper on "The Practical Operation of a Dynamometer Car in Establishing Locomotive-Tonnage Rating." The paper described in detail the investigations carried on by the speaker for the Boston and Maine Railroad.

After some discussion the meeting adjourned, the chairman first expressing the thanks of the Society to the speaker for his excellent paper.

SAMUEL C. PRESCOTT, *Secretary.*

ANNUAL REPORT OF THE EXECUTIVE COMMITTEE PRESENTED AT THE FORTY-FOURTH ANNUAL MEETING OF THE SOCIETY, MAY 10, 1906

The first meeting of the SOCIETY OF ARTS for the present year was held on October 12, 1905. Thirteen meetings have been held, with an average attendance of one hundred and seventeen. During the past year the interest awakened in the Society and manifest for several years has been continued, not only by the members, but especially by the public at large and many of the students of the Institute. The attendance of the latter when papers of technical interest have been presented was especially gratifying. The range of the subjects which have been presented has been a wide one, and as a consequence nearly all the students have had the opportunity to hear a paper on some subject of professional interest.

The following papers have been read:

"Disposal of City Sewage," by Professor Charles-Edward A. Winslow, Biologist-in-Charge of the Research Station and Sewage Experiment Laboratory.

"Brown-tail and Gypsy Moths: Their Life Histories, and Some Suggestions for Their Suppression," by Mr. William Lyman Underwood.

"Submarine Signaling," by Mr. Henry R. Gilson.

"Recent Researches on the Canals of Mars," by Professor Percival Lowell, Director of the Astronomical Observatory at Flagstaff, Arizona.

"The Treatment of the Black Sands of the Pacific Coast by the United States Geological Survey," by Professor Robert H. Richards, of the Institute.

"The American Indian Folklore," by Professor Alexander F. Chamberlain, of Clark University.

"Hydraulic Mining in British Columbia and Alaska," by Mr. Howard W. Dubois, Mining Engineer of Philadelphia.

"Causes and Effects of River Capture," by Professor Douglas W. Johnson, of the Institute.

"Shoddy, or the History of a Woolen Rag," by Mr. Henry G. Kittredge, Editor of the *Textile American*.

"The Chemistry of Cellulose as Applied to Textile Fibres, Mercerized Cotton, Artificial Silk, and Horse Hair," by Professor William H. Walker, of the Institute.

"The American Bison, Our Grandest Native Animal," by Mr. Ernest Harold Baynes.

"The Rationale of the Industrial-Betterment Movement," by Mr. H. F. J. Porter, of New York.

"Practical Operation of a Dynamometer Car in Establishing Locomotive-Tonnage Rating," by Mr. Herbert O. Keay.

The number of members of the Society has remained practically the same as last year. Fifteen members have resigned, two have died and two have not been heard from, and the number of new members elected to Associate Membership has been fourteen, leaving the total membership three hundred and fifty-eight.

The TECHNOLOGY QUARTERLY has continued its publication under the editorship of Dr. Robert P. Bigelow, with the advice and counsel of the Publication Committee of the Society. In addition to the Proceedings of the Society twenty-five papers and twenty-five book reviews have been published. Among the papers published were some of special interest.

Professor John Bigelow, Jr., has published a paper on "Modern Language Teaching, with Special Reference to Pronunciation and Conversation."

Professor Hovgaard has published two papers, one on "The Cruiser," and another, "The Sea-Going Battleship."

Mr. Henry R. Gilson has published a paper on "Submarine Signaling."

Mr. F. F. Fowle a paper on "Railway Telephone Service, the Cost of Line Construction."

Mr. William Atkinson a paper on "Orientation of Buildings and Streets in Relation to Sunlight."

The different departments have contributed papers as follows: Biological Department, four papers; Chemical Department, three papers; Electrical Engineering Department, two papers; Geological

Department, two papers; Naval Architecture Department, two papers; Modern Languages Department, one paper.

Respectfully submitted,

GEORGE W. BLODGETT,
JAMES P. MUNROE,
CHARLES T. MAIN,
E. H. HEWINS,
S. C. PRESCOTT,
} *Executive Committee.*

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS[1]

INTRODUCTION: OUTLINE OF THE INVESTIGATION
PART I. PREPARATION OF THE SOLUTION
PART II. ANALYSIS OF THE SILVER, COPPER, AND TIN GROUPS

By ARTHUR A. NOYES and WILLIAM C. BRAY

INTRODUCTION: OUTLINE OF THE INVESTIGATION

This investigation was undertaken for the purpose of studying the processes of qualitative analysis in general use, with reference to their effectiveness in enabling small quantities of each of the more common elements or element-groups to be detected in the presence of any of the other elements, and for the purpose of selecting the methods best adapted to this end and of improving them wherever desirable and practicable. In spite of the vast number of text-books on qualitative analysis in which more or less different processes are recommended, there seems to have been made in recent years no exact systematic study of the relative effectiveness of the separations or of the delicacy of the final tests. It has seemed to us, therefore, worth while to make a detailed investigation of this kind; and as a result of it to develop, if possible, a system of analysis which will enable a quantity of any element as small as one or two milligrams to be detected in any mixture. Effort will also be made to employ only such processes as enable a rough estimate to be made of the quantity of the various elements present; for this is usually a more important function of a good qualitative analysis than the mere determination of their presence or absence. To this end tests of excessive delicacy, like certain color reactions, will be avoided, and each element will be obtained in the solid form as a precipitate or residue, as far as possible.

Especial attention will also be devoted to the chemical reactions involved in the process and to the explanations of them furnished by

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the Mass-Action Law and Ionic Theory. Since the first systematic application of modern theories to analytical chemistry was made by Ostwald, many physico-chemical researches have been published which make it possible to give such explanations with certainty in a greater number of cases. References to the more important articles relating to the chemistry of the processes and to their theoretical interpretation will be given.

The elements and element-groups included in this system of analysis are primarily those which, with remarkable unanimity, are treated of in the ordinary schemes of qualitative analysis; but we have also introduced the more important of the so-called rare elements, in so far as this has seemed practicable without seriously complicating or modifying the process best adapted to the more common elements. An independent "System of Qualitative Analysis Including Nearly All the Metallic Elements" is also being worked out in this laboratory; and parts of it have already been published under this title in this QUARTERLY. The latter scheme differs from the one here presented in that the detection of the rare elements forms the essential feature, instead of a merely incidental one.

The results will be presented in the form that seems best adapted to the purposes of the analyst. The "System of Analysis" is for convenience in publication primarily divided into a series of parts, each of which treats of one of the large divisions of the subject. Under each part is first presented a "General Discussion," in which are given the reasons for the adoption of the process employed. This is followed by a "Tabular Outline," which gives a survey of the important steps and the chemical reactions involved in the process of analysis. Then comes the chapter entitled, "Procedures and Notes," in which the details of the process are presented and discussed. Next are given the "Test Analyses," which were made with known mixtures in order to test the efficiency of the process. Finally are presented "Confirmatory Experiments and References," which serve to substantiate the statements made in the notes and to justify the details of the procedures.

In the procedures the operations are described in much detail; it is, however, assumed that the analyst is familiar with the manipulative processes of exact qualitative analysis and with the ordinary precautions for assuring completeness of precipitation, washing, etc. In the notes are explained the purposes of the operations and the specific chemical

reactions involved from the point of view of the Mass-Action Law and the Ionic Theory, with the general principles of which the reader is assumed to be acquainted. The directions are almost always given in the form applicable to the case where all elements that might be present are present, the modifications admissible when certain operations lead to negative results being usually sufficiently evident. The scheme consists of a series of numbered "Procedures," a new one being begun whenever the substance has been resolved into two parts (such as a precipitate and filtrate) which are to be submitted to different operations. Procedures which are devoted to the detection or separation of the rarer elements are preceded by an asterisk, and are further designated by a letter attached to the procedure number: they may be omitted if such elements are not to be tested for. Notes under other procedures, when they relate to such elements, are also distinguished by an asterisk. At the beginning of each procedure the one by which the substance was last treated, and at the end of each procedure those by which the two separated portions of it are next to be treated, are referred to by number.

Most of the experiments described under "Confirmatory Experiments and References" are undoubtedly merely confirmations of previously known chemical facts. The application of these facts to the specific conditions of the procedures it was, however, constantly necessary to test; and it has seemed worth while to make the results a matter of record. The experiments are preceded by a reference to the procedure and note to which they relate.

Of the abbreviations employed only a few need be explained: G. D. is used for General Discussion; P. for Procedure; N. for Note; C. E. for Confirmatory Experiments; T. A. for Test Analyses. A number within parentheses expresses the specific gravity at 15°. When it is directed to add a variable quantity of a reagent (for example, 5–15 ccm.), the amount used should be adjusted to the size of the precipitate or residue.

The metallic elements have been classified in "Groups" on the basis of their behavior toward the general ("group") reagents, and these groups are designated and defined as follows, the rarer elements here considered being indicated by an asterisk: *silver group*, elements precipitated wholly or in part by hydrochloric acid (Ag, Pb, Hg [mercurous], *Tl); *copper group*, elements precipitated by hydrogen sulphide from weakly acid solution whose sulphides remain undissolved

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in large quantity by yellow ammonium sulphide (Hg [mercuric], Pb, Bi, Cd, Cu, *Au, *Pt); *tin group*, elements precipitated by hydrogen sulphide from weakly acid solution whose sulphides dissolve readily or in considerable quantity in yellow ammonium sulphide (As, Sb, Sn, *Au, *Pt, *Se, *Te, *Mo); *iron group*, elements not precipitated by hydrogen sulphide from acid solution, but precipitated by ammonium hydroxide and sulphide (Co, Ni, Fe, Mn, Cr, Al, Zn, *Ti, *Zr, *U, *V, *Be); the *alkaline-earth group*, elements not precipitated by any of these reagents, but precipitated by ammonium carbonate (Ba, Sr, Ca); the *alkali group*, elements not precipitated by any of the preceding reagents (Mg, Na, K, *Li).

PART I. PREPARATION OF THE SOLUTION

General Discussion

The attempt has been made to devise a systematic method of preparing the solution of the substance for analysis, which shall be uniform for all substances, which in the case of those ordinarily met with shall be as rapid as possible, and which shall be so complete as to effect the solution of substantially all known substances. Heretofore little attention has been given to the development of such a definite, uniform plan of treatment, it being assumed that the analyst has the experience necessary to enable him to select, on the basis of the known general character of the substance or of a series of preliminary tests in the dry way, the most suitable method to employ for its decomposition. Yet more experience is required for this than for the ordinary group separations; and there seems to be no reason whatever why this important and difficult part of the analytical process should not be treated in the same systematic way as are the separations and tests for the various elements.

The general character of the plan here presented for accomplishing this end will be readily seen from the "Tabular Outline" given below. The only preliminary test required is one for the presence of organic matter and water, which is made by heating the substance in a closed tube; thus are eliminated the time-consuming blowpipe tests usually recommended, the success of which can be assured and the true significance interpreted only after much experience. For substances found to

contain organic matter a special treatment with nitric and sulphuric acids is described by which the organic matter is destroyed. Other substances are treated first with water, and, if this does not cause complete solution, immediately after with fairly strong nitric acid; and any residue still remaining is boiled with hydrochloric acid and *aqua regia*, in order to remove a few substances, such as manganese and lead peroxides, mercuric sulphide, gold, and platinum, which are attacked by these acids, but not by nitric acid.

In the treatment of the residue that may remain unattacked by these acids lies the main difference between our process and that ordinarily recommended in text-books on qualitative analysis; for, as shown in Table II, any such residue is heated with sulphuric and hydrofluoric acids instead of being fused with an alkaline carbonate. By this modification the process of preparing the solution is much simplified in the great majority of cases; for silica is thereby detected and eliminated at the start, and almost all silicates are decomposed, yielding at once either a complete solution, or, if lead, barium, strontium, or much calcium is still present, a residue of their sulphates which can readily be decomposed by boiling with sodium carbonate solution. An even more important advantage of this method, however, is that no foreign metallic elements are introduced; while, when a fusion is made, alkali elements are introduced from the flux, and aluminum, calcium, and silica from the porcelain crucible, which ordinarily must be used, owing to the possible presence of reducible metallic elements, thus making it necessary to employ other special methods for the detection of these elements. Objection may be raised to the use of hydrofluoric acid because of its being an expensive and irritating reagent and because it must be handled in platinum vessels, thus making it hardly practicable for the use of large classes of beginners in the subject. Realizing the force of the last consideration, we have described (as indicated in Table III) the usual method of fusion with an alkaline carbonate as an alternative procedure, which may be used under circumstances which do not permit of the simpler and more satisfactory method with hydrofluoric acid. But in doing so we wish to express the conviction that when the subject of qualitative analysis is studied as a branch of analytical chemistry, and not merely as a means of imparting a certain additional chemical knowledge, it ought to be pursued under the same conditions with respect to accuracy of manipulation and availability of facilities as is customary in courses upon quantitative analysis. For

the inability to make a good qualitative analysis is a common source of error in quantitative analytical results; and lack of thoroughness in the instruction in qualitative analysis often develops careless and inaccurate habits of work. We have therefore aimed to develop the scheme of analysis best adapted to the purposes of the analyst, and have not hesitated to avail ourselves of the special methods and reagents commonly used only in quantitative work when a more reliable or simpler process could thereby be developed.

Only few substances, especially a few silicates and native oxides, fail to be dissolved by the treatment with sulphuric and hydrofluoric acids; and it is very rare that any further operations are necessary. But to provide for these special cases it is directed to fuse any residue with alkaline carbonate and nitrate, which can now safely be done in a platinum crucible; and, finally, to fuse any residue still remaining (which is likely to consist only of aluminum, tin, or titanium oxide) with potassium hydroxide.

Tabular Outline

In the "Tabular Outlines" the enclosure of a symbol in brackets shows that the element may divide itself between the residue and solution in the operation immediately preceding. The symbols of the anhydrous substances are given, without reference to the actual state of their hydration in the residue or precipitate.

TABLE I

Determine by preliminary tests whether the substance contains organic matter (P. 1); and if not, whether it dissolves completely in water and forms an acid or neutral solution (P. 3).

<table>
<tr>
<td colspan="3">SUBSTANCES CONTAINING ORGANIC MATTER.
Heat with H_2SO_4 and HNO_3 to destroy organic matter, evaporate off HNO_3, add water (P. 2).</td>
<td colspan="2">SUBSTANCES SOLUBLE IN WATER FORMING A NEUTRAL OR ACID SOLUTION.
Dissolve in water, add HCl (P. 11).</td>
<td colspan="4">OTHER SUBSTANCES.
Heat with HNO_3, evaporate, dry, add dilute HNO_3 (P. 3).</td>
</tr>
<tr>
<td rowspan="2">Residue.
See Table II or III below.</td>
<td colspan="2">Solution:
Add HCl (P. 2).</td>
<td rowspan="2">Precipitate:
AgCl, HgCl, [$PbCl_2$], [TlCl]
(P. 12).</td>
<td rowspan="2">Filtrate:
All elements except Ag.
Pass in H_2S (P. 21).</td>
<td colspan="2">Solution:
Add HCl (P. 3).</td>
<td rowspan="2">Residue: A. From alloys: Sb_2O_5, SnO_2, [P_2O_5], [As_2O_5], SiO_2, [TiO_2], WO_3, C, Au, Pt, Ir, etc.; some iron alloys.
B. From other substances: oxides under A above and substances under B in Table II; also MnO_2, PbO_2, and HgS.
Heat with HCl and HCl + HNO_3, evaporate, dry, add dilute HCl (P. 4).</td>
</tr>
<tr>
<td>Precipitate:
AgCl.
Confirm by P. 15.</td>
<td>Filtrate:
All elements except Ag, Cr, Pb, Ba, Sr. Pass in H_2S (P. 21).</td>
<td>Precipitate:
AgCl, [$PbCl_2$], [TlCl]
(P. 12).</td>
<td>Filtrate:
Evaporate; add HCl (P. 4).</td>
</tr>
<tr>
<td colspan="7"></td>
<td>Solution:
All elements except Ag. Pass in H_2S (P. 21).</td>
<td>Residue. See Table II or III below.</td>
</tr>
</table>

TABLE II

RESIDUE UNDISSOLVED BY ACIDS FROM TABLE I

A. From alloys: [SnO_2], SiO_2, TiO_2, WO_3. (C, Ir, etc., some Fe alloys.)[1]

B. From nonmetallic substances: oxides under **A**; also AgCl, CaF_2, MoS_2, many silicates, the sulphates of Pb, Ba, Sr, native Al_2O_3, $FeO.Cr_2O_3$.

C. From substances containing organic matter: substances under **B** (except CaF_2); also Sb_2O_5, $BiOSO_4$, $Cr_2(SO_4)_3$, $CaSO_4$.

Heat with H_2SO_4 and HF, evaporate to expel HF, dilute, boil (P. 5).

<table>
<tr><td rowspan="5">Gas: SiF_4.
PRESENCE OF SILICON.</td><td rowspan="5">Solution:
All elements except Pb, Ba, Sr.
Pass in H_2S (P. 21).</td><td colspan="3">Residue: Pb, Ba, Sr, [Ca], [Bi], [Cr] as sulphates; Sb_2O_5, WO_3; native SnO_2, Al_2O_3, TiO_2, $FeO.Cr_2O_3$; some silicates. Boil with Na_2CO_3 solution (P. 6).</td></tr>
<tr><td rowspan="4">Solution:
Na_2WO_4.
Test for tungsten (*P. 6a).</td><td colspan="2">Residue: Pb, Bi, [Ba], Sr, Ca as carbonate; [$BaSO_4$], other substances except WO_3 as above. Heat with HCl (P. 6).</td></tr>
<tr><td rowspan="3">Solution:
Pb, Bi, Sb, Cr, [Ba], Sr, Ca as chlorides. Pass in H_2S (P. 21).</td><td colspan="2">Residue: [$Cr_2(SO_4)_3$], [$BaSO_4$], MoS_2, native oxides and silicates as above. Fuse with Na_2CO_3 and KNO_3, add HCl, evaporate, add dilute HCl (P. 7).</td></tr>
<tr><td>Solution: Test for all elements except alkalies (P. 21).</td><td>Residue: SiO_2; native SnO_2, TiO_2, Al_2O_3. Remove SiO_2 with HF; fuse residue with KOH (P. 7, N. 3).</td></tr>
</table>

[1] A *metallic* residue obtained from an alloy is not treated as described in the table, but is best fused with Na_2O_2 (P. 4, N. 2).

TABLE III

(Alternative Process)

RESIDUE UNDISSOLVED BY ACIDS FROM TABLE I

Composition: See Heading of Table II

Fuse with Na_2CO_3 and K_2CO_3 in a porcelain crucible, adding KNO_3 if necessary; add water, filter (*P. 8*).

Solution: Sodium and potassium silicate, stannate, antimonate, arsenate, aluminate, chromate, manganate, tungstate, molybdate, sulphate, and carbonate. *Acidify, evaporate, dry, add dilute HCl* (*P. 8*).

Solution: Sn, Sb, As, Mo, Al, Cr, as chlorides. *Pass in H_2S* (*P. 21*).

Residue: SiO_2, WO_3. *Reject or treat by P. 5 and *6a.*

Residue: Almost any metallic element as metal, oxide, or carbonate. *Add HNO_3* (*P. 8*).

Solution: Almost any element as nitrate. *Add HCl* (*P. 8*).

Filtrate: *Evaporate, add HCl, test for all elements except alkalies* (*P. 21*).

Precipitate: AgCl, [$PbCl_2$] (*P. 12*).

Residue: Native SnO_2, TiO_2, Al_2O_3. *Fuse with KOH, add water and HCl* (*P. 7, N. 3*), *test solution for Sn, Al, Ti.*

Procedures and Notes

Procedure 1. — If the substance is a solid, note its color, odor, and texture; examine it with a lens to determine whether it appears to be heterogeneous, and, if so, note the appearance of its constituents. Note especially whether it is an alloy or a nonmetallic substance. If the substance is an alloy, pass to P. 3. If the substance is not an alloy, to determine whether organic matter or water is present in it, heat gently at first, then strongly, about 0.1 gram of the finely powdered substance in a hard glass tube (of about 0.6 cm. bore and 8 cm. length) closed at one end. Note whether the substance blackens, whether a tarry or aqueous deposit forms on the cold part of the tube, and whether a burnt odor is emitted. If organic matter is thus proved to be absent, pass to P. 3; if proved to be present, pass to P. 2.

If the substance is a solution in water or other volatile liquid, note its odor, test it with litmus paper, and evaporate just to dryness enough to yield a residue of about 1 gram. Test a small quantity of this residue as described in the preceding paragraph. Treat the remainder by P. 3 if organic matter is found to be absent; otherwise, by P. 2.

Notes. — 1. When a complete analysis in the wet way is to be made, it is usually not worth while to make a more extended preliminary examination in the dry way. The closed-tube test is, however, essential, in order to show whether organic matter or water is present; and incidentally it often furnishes other valuable information.

2. Certain kinds of organic matter, especially sugars and hydroxy-acids such as tartaric, citric, and lactic acids, prevent the precipitation of the hydroxides of aluminum and chromium in the subsequent analysis, and must therefore be detected and removed. Moreover, a large quantity of organic matter of any kind interferes with the execution of the analysis; for example, with the operations of solution, filtration, and evaporation. . Alloys do not contain organic matter or water; and therefore the closed tube test need not be applied to them.

3. The closed tube test is a more satisfactory method of detecting organic matter than heating in an open vessel. Blackening, unless accompanied by a burnt odor, or by the formation of a tarry deposit, is not due to organic matter. Copper, cobalt, and nickel salts may cause it, owing to the formation of the black oxides on heating.

4. It is usually desirable to determine whether water is a constituent of the substance, and, if so, whether it is present in large or small pro-

portion. This can be done with a fair degree of delicacy by the closed tube test, provided care be taken to keep the upper part of the tube cool during the first of the heating. Water may be present as so-called water of constitution, as in FeO_3H_3 or Na_2HPO_4; as water of crystallization, as in $MgSO_4.7H_2O$; as enclosed water, as in some hydrated silicates like the zeolites or as mother liquor within crystals; and as hygroscopic moisture on the surface. Water of constitution may be expelled only at a fairly high temperature, while in the other forms it is seldom retained above 200°.

5. The closed tube test may also furnish evidence of the presence of certain metallic and nonmetallic elements when they are present in considerable quantity. Thus all ammonium salts and mercury compounds are volatilized much below a red heat: the former give on the upper part of the tube a white sublimate; the chlorides of mercury also give a white sublimate; while most other mercury compounds give a gray one, consisting of minute globules of mercury, made visible by a lens or by rubbing with a wire. Uncombined As, As_2O_3, and As_2S_3 are also readily volatilized, forming black, white, and yellow sublimates, respectively. Of the acid-forming elements or groups, free sulphur or a persulphide is shown by a sublimate of reddish brown drops, changing to a yellow solid on cooling, and accompanied by odor of SO_2; a moist sulphide, by the odor of H_2S; a nitrate or nitrite, by brown vapors of NO_2; free iodine or a decomposable iodide, by a black sublimate of I_2 and by its violet vapor; a sulphite, by the odor of SO_2; a peroxide, chlorate, or nitrate, by evolution of oxygen, recognized by its inflaming a glowing wood-splinter held in the tube; and a carbonate or oxalate, by the evolution of CO_2, recognized by its causing turbidity in a drop of $Ba(OH)_2$ solution.

6. If the substance to be analyzed is a liquid, it is desirable to determine first how much, if any, solid substance is present in it; for enough must be taken for analysis to enable small quantities of the metallic elements to be detected. Moreover, if it is dissolved in a volatile organic solvent the latter is removed by evaporation.

Procedure 2. — If the closed tube test (P. 1) has shown the presence of organic matter, powder, or cut into small pieces, 1 to 5 grams of the substance (according to the quantity of organic matter present) Add to it in a casserole about 5 ccm. H_2SO_4 (1.84); warm gently until the substance is well charred; cool; add slowly, with constant stirring, under a hood, HNO_3 (1.42), until violent reaction ceases; digest for a few minutes on a steam bath, and then heat over a flame, keeping the dish moving, until the substance is thoroughly charred. Cool, again add HNO_3 as before, and heat until thick fumes of H_2SO_4

are evolved; cool somewhat, and add a little HNO_3. Repeat this process till the H_2SO_4 becomes light-colored and remains so when heated strongly.

Evaporate the remaining H_2SO_4 under a hood to about 1.5 ccm. Cool and add carefully about 10 ccm. water. If there is a residue, cover the casserole and boil the mixture (to extract slowly dissolving sulphates); cool, filter, and wash, first with H_2SO_4 (1.20) and then with a little water, rejecting the washings. (Residue, P. 5.) To the solution add a drop of HCl (1.12). (If a precipitate forms, add more HCl, but only as long as a precipitate continues to separate; filter, wash the precipitate, and test it for silver by P. 15.) Dilute the solution to a volume of 40 ccm. (Solution, P. 21.)

Notes. — 1. This method of destroying organic matter is of very general application, being effective even when such stable substances as paraffin are present. Organic matter can also be destroyed by ignition, but this has the disadvantages of volatilizing certain elements, especially mercury and arsenic, and of making some substances very difficultly soluble. When the organic matter consists only of oil, as is the case with an oil paint, it may be better to extract it with ether, especially when it is desired to determine the proximate constituents of the substance.

2. The residue contains: any substances originally present that have not been attacked by HNO_3 or H_2SO_4, especially silicates; all the lead, strontium, and barium that may have been present in any form, since the sulphates of these elements are insoluble in dilute H_2SO_4; all the silica, since silicic acid is dehydrated and made insoluble by heating with H_2SO_4; some of the calcium, bismuth, antimony, and tin, when these elements are present in moderate quantity, since their sulphates (or oxides) are not readily soluble in dilute H_2SO_4; and substantially all of the chromium, since its sulphate is converted into the insoluble anhydrous form.

3. After the organic matter is destroyed, the solution is evaporated to about 1.5 ccm. and the solution is finally diluted to 40 ccm., in order that the concentration of the acid may be right for the subsequent H_2S precipitation.

Procedure 3. — If organic matter is absent (P. 1), reduce the substance to a finely divided form (as described in N. 1); weigh out into a casserole about 1 gram if it is a nonmetallic substance, or about 0.5 gram if it is an alloy.

In case the substance is not an alloy, add to it 10–30 ccm. water,

heat to boiling, and test the solution with litmus paper. If the substance has dissolved completely and the solution is neutral or acid, treat the solution by P. 11. If there is a residue or if the solution is alkaline, add carefully without filtering 5–10 ccm. HNO_3 (1.42), and evaporate just to dryness.

In case the substance is an alloy, pour over it 10 ccm. HNO_3 (1.20), cover the dish with a watch glass, heat the mixture on a steam bath as long as any action continues, adding a little HNO_3 (1.42) if action is renewed thereby, or a little water if crystalline salts have separated, and then evaporate just to dryness.

Heat the residue obtained in either case at 120–130° until it is perfectly dry, by keeping the casserole in motion over a flame, or, better, by heating it in a hot closet at that temperature for at least half an hour. Loosen the dehydrated residue from the dish and rub it to a fine powder with a pestle; add to it 5–10 ccm. HNO_3 (1.20), cover the dish, and heat on a steam bath for 10 minutes. Dilute with 20 ccm. water, heat to boiling, filter, and wash the residue. (Residue, P. 4.) To the solution add 5 ccm. HCl (1.20) to precipitate the silver group, filter, and wash the precipitate with a little cold water, adding the washings to the filtrate. (Precipitate, P. 12; filtrate, P. 4, second paragraph.)

Notes. — 1. In order that in the following procedures difficultly soluble substances may be dissolved, the substance must be reduced to a very fine powder. This is usually best accomplished by grinding the substance, in small quantities at a time, in a mortar. With hard substances, and in general with minerals, an agate mortar should be used. Most alloys cannot be powdered in this way; these may be converted into a form that offers a large surface by hammering in a steel mortar, filing with a fine steel file, shaving with a knife, or converting into turnings with a lathe.

2. The quantity of the substance taken for analysis should always be approximately known; for a good qualitative analysis should show, not merely the presence or absence of the various elements in the substance, but should enable their relative quantities to be estimated. Since 1–2 mgm. of almost any element can be detected by this system of analysis, the presence of 0.1–0.2% of an element will be detected when a gram of substance is taken, and this degree of delicacy is ordinarily sufficient. If much more than this quantity is taken, the precipitates may be so large that much time is consumed in filtering and washing them. For this reason it is best to use only about half a gram of an

alloy, since, owing to the absence of acid radicals, the same quantity of metallic elements is contained in a less amount of substance.

3. When the substance dissolves only partly in water, it is not worth while to filter off the residue and analyze it and the solution separately, unless special information in regard to the soluble constituents is desired. If, therefore, it is known to be partly insoluble in water, it is best treated at once with HNO_3, as is directed in the case of an alloy. If, however, it is completely soluble in water, the addition of HNO_3 is avoided, since it would have to be removed before the subsequent precipitation with H_2S.

4. If the aqueous solution has an alkaline reaction, the addition of an acid may cause precipitation of any substance held in solution by an alkaline solvent; for example, sulphur or sulphides of the tin group from an alkaline sulphide solution; silver chloride or cyanide from a potassium cyanide solution; silicic acid from sodium silicate solution; or metallic hydroxides from solutions in alkalies. An alkaline solution should, therefore, not be treated directly with HCl by P. 11, for the precipitate formed might contain other substances than chlorides of the silver group.

5. An acid reaction of the aqueous solution is due to hydrogen ions, which may arise from free acid, from an acid salt of a strong acid, or (by hydrolysis) from a neutral salt of a strong acid and a weak base. An alkaline reaction is due to hydroxide ions, which may arise from a soluble hydroxide, or (by hydrolysis) from a carbonate, sulphide, phosphate, borate, cyanide or a salt of some other weak acid. It is to be noted that the terms "acid salt" and "neutral salt" refer only to the extent of the replacement of the hydrogen of the acid by the metallic element, and do not show the reaction towards litmus or other indicators. This reaction depends on the presence of a sufficient concentration of hydrogen or hydroxide ions to affect the indicator employed. Thus the neutral salts Na_2CO_3, Na_2S, etc., and even the acid salts $NaHCO_3$, Na_2HPO_4, react alkaline with litmus; while some other neutral salts, such as $Al(NO_3)_3$, react acid.

6. When an acid is added to a nonmetallic substance or its aqueous solution, the evolution of any gas and its odor should be noted, since this indicates the nature of the acid radical present. Thus carbonates evolve CO_2; sulphides, H_2S; sulphites, SO_2; and cyanides, HCN. On boiling the HNO_3 solution, the presence of sulphides is further indicated by the separation of sulphur as a spongy or pasty mass, which floats on the surface and may be removed by means of a spatula or rod; and the presence of iodides is shown by the liberation of free iodine, which may separate as a black precipitate, which imparts a brown color to the solution, and which gives rise to violet vapors above it.

7. In dissolving nonmetallic substances either HNO_3 or HCl may be first used, each having advantages and disadvantages of its own. HNO_3 dissolves, owing to its oxidizing power, many alloys and sulphides not attacked by HCl, but fails to dissolve certain oxides, especially MnO_2, Sb_2O_5, and hydrated SnO_2, which dissolve in HCl. HCl may cause the precipitation of chlorides of the silver group; while strong HNO_3 on heating oxidizes sulphides partially to sulphates, and may cause the precipitation of lead, barium, strontium, and calcium sulphates; thus in either case making it sometimes impossible to determine whether complete decomposition has resulted. HNO_3 oxidizes mercurous, arsenous, antimonous, stannous, and ferrous compounds to the higher state of oxidation; consequently almost all the antimony and tin will usually be found in the residue insoluble in dilute HNO_3 after evaporation, all the mercury will be in the H_2S precipitate, and sulphur will always be precipitated by H_2S when iron is present. When HCl is used as a solvent, mercury, selenium, and arsenic in the arsenous form would be wholly or partly lost, owing to the volatility of their chlorides, in the subsequent evaporation, which is necessary in order to remove silica. For this last reason, and for the reason that the procedure is a more general one in that it provides for the solution of alloys and of a larger proportion of nonmetallic substances and for the isolation of the silver group, the use of HNO_3 is here recommended. In special cases it is advantageous to use dilute HCl instead of HNO_3, especially when the substance dissolves completely in HCl and it is not necessary to evaporate the solution to remove silica.

8. When a silicate is decomposed by acid, silicic acid may separate as a gelatinous precipitate, but even then a part of it always remains in solution, mainly as a colloid. When thoroughly dried at 100–130°, it is partially dehydrated and becomes entirely insoluble. The HNO_3 acid solution is therefore evaporated to dryness and the residue is heated at 120–130°, in order to remove the silica at this point; for, if it were not removed, it would appear as a gelatinous precipitate at some later stage of the analysis; thus, if it did not separate earlier, it would be precipitated by NH_4OH together with the iron group and might then be mistaken for aluminum hydroxide. In the case of nonmetallic substances which cannot contain silica, the evaporation and heating at 120–130° may be omitted.

9. With reference to the treatment of alloys with HNO_3 the following facts should be borne in mind. All the more common elements are dissolved by strong HNO_3 except antimony, tin, and silicon. These are oxidized to antimonic acid ($Sb_2O_5.nH_2O$), metastannic acid (nH_2SnO_3), and silicic acid, which separate at once as white amorphous precipitates

except when only small amounts of these elements are present. Certain nitrates, especially that of lead, may separate in crystalline form from the strong HNO_3, but these dissolve upon adding water and heating to boiling. * Of the more important rarer elements, titanium and tungsten, like antimony and tin, separate in the form of insoluble hydroxides; in the case of tungsten, tungstic acid (H_2WO_4) separates as a dense precipitate of a yellow color.

10. In the case of an alloy the evaporation to dryness and heating at 120–130° serve to partially dehydrate the hydroxides of silicon, tin, antimony, titanium, and tungsten, whereby they are rendered nearly insoluble in HNO_3, and thus make possible a conclusion in regard to their presence or absence. If after having thoroughly dried the mixture at this temperature there is no residue insoluble in the HNO_3 (1.20), it shows the absence of silicon, tin, and tungsten in quantity as large as 1 mgm., and that of antimony and titanium in quantity as large as 2 or 3 mgm. The fact must not be overlooked, however, that in the dehydrated form even a very small residue or slight turbidity may correspond to an appreciable quantity of one of these elements. Therefore, if no residue can be seen, rub the sides of the dish gently with the rubber-covered end of a glass rod, pour into a small flask, allow the liquid to stand 2 or 3 minutes, and note whether there is any residue whatever. The knowledge that tin is absent is helpful, since the subsequent procedures for the detection of this element may be omitted. The subsequent procedures for antimony may, in the absence of a residue, also be omitted, provided quantities as small as 3 mgm. are not to be tested for. In addition to the hydroxides named above the residue may also contain a considerable quantity of stannic phosphate or arsenate when tin and phosphorus or arsenic are simultaneously present, or of bismuth hydroxide when both antimony and bismuth are present; also small quantities of various other elements enclosed in a residue consisting of those already mentioned.

11. The hydroxides referred to in the last two notes usually separate also in the treatment of nonmetallic substances with HNO_3 when the corresponding elements are present; but the nonexistence of a residue must not, except in the case of silicon, be regarded as conclusive evidence of their absence in such substances. For acid radicals may be present which by combination with the hydroxides cause them to remain in solution; thus the presence of chloride or sulphate might cause a considerable quantity of tin, antimony, or titanium to dissolve, while that of phosphate might lead to the solution of even a large quantity of tungsten.

12. A black or metallic residue insoluble in HNO_3, obtained in the case of an alloy, may contain carbon or carbides, certain alloys of iron, such as ferrochrome or ferrosilicon, gold, or any of the platinum metals. If there is no such residue, it shows the absence of gold and platinum.

13. If the substance is nonmetallic, the residue insoluble in HNO_3 probably consists of one or more of the following substances: the partially dehydrated hydroxides of tin, antimony, silicon, titanium, and tungsten; the native or ignited oxides of the same elements, of aluminum, and of chromium; anhydrous chromic salts; the peroxides of manganese and lead; the sulphates of barium, strontium, and lead; the sulphides of mercury and molybdenum; silica; the silicates and fluosilicates of many elements; fluoride of calcium; the halides of silver and lead; the phosphates of tin and of rare earths; ferrocyanide of iron; sulphur; carbon; silicon carbide.

14. In regard to the precipitation of the silver group by HCl, see notes on P. 11.

Procedure 4. — To the residue insoluble in HNO_3 (P. 3) in a casserole add gradually 5–10 ccm. HCl (1.20), and heat as long as action continues, adding more acid if necessary. If the substance does not dissolve completely in HCl, add to the mixture without filtering one-third its volume of HNO_3 (1.42), and heat gently as long as action continues, adding more of the acids if necessary.

To this solution in HCl alone, or in HCl and HNO_3, without filtering off any residue, add the filtrate obtained in P. 3, and evaporate the mixture nearly to dryness. In order to expel the HNO_3, moisten the residue with 2–5 ccm. HCl (1.20), and evaporate to dryness. Thoroughly dry the residue by heating it at 120–130° in a hot closet or by keeping it in motion over a small flame. Add to the residue 4 ccm. HCl (1.12), measured in a small graduate, and about 20 ccm. water; boil gently for a few minutes if there is a residue; filter, and wash the residue thoroughly with boiling water. Pour the filtrate into a graduate and add enough water to make its volume 40 ccm. (Residue, if nonmetallic, P. 5, if metallic, P. 4, N. 2; solution, P. 21.)

Notes. — 1. Of the substances that may be present in the residue undissolved by HNO_3 (see P. 3, N. 12 and 13) the peroxides of manganese and lead are reduced and dissolved by concentrated HCl; antimonic acid, stannic phosphate, and much metastannic acid are also dissolved by it. Upon the addition of HNO_3, whereby the strongly oxidizing mixture known as *aqua regia* is produced, gold, platinum, and mercuric sulphide are entirely dissolved; and silver compounds, such as AgBr, AgI, and AgCN, are converted into AgCl. The chloride of silver and the sulphates of strontium and lead dissolve in large quantity in the concentrated acids, but only in much smaller quantity in the small amount

of dilute HCl added after the evaporation. Some of the other substances that may be in the residue, especially the oxides and certain silicates, are slowly attacked by the strong acids, but the solvent action is not rapid enough to make this a practicable method.

2. If the original substance was an alloy, a residue after the treatment with HCl and HNO_3 probably consists, if nonmetallic, only of metastannic, silicic, titanic, or tungstic acid; if black or metallic, of carbon, a platinum metal, or an alloy of iron with chromium, silicon, etc. If nonmetallic, it is treated with H_2SO_4 and HF by the regular procedure, in order to test for and remove silica and to dissolve metastannic and titanic acids. If metallic, such a treatment would not effect solution; the residue is then best fused with Na_2O_2 in a nickel crucible, the mass treated with water and HCl, and the solution analyzed as usual, except that nickel cannot be tested for. For a description of this process and the results attained by it, see A. A. Noyes, "System of Qualitative Analysis Including Nearly All the Metallic Elements," Part I, Procedure 13, published in this QUARTERLY, **16**, p. 113 (1903).

3. The solution is evaporated to render insoluble silicic acid which may have come from the decomposition of silicates, and to remove the large quantity of acid which would otherwise interfere with the H_2S precipitation. The evaporation with HCl serves, moreover, to remove HNO_3, which, if present in large quantity, would destroy the H_2S with liberation of sulphur. Since the success of the separation by H_2S of the copper and tin groups from the iron group requires a proper concentration of acid in the solution, a measured quantity of HCl is added and the solution is diluted to a definite volume.

4. If the original substance was an alloy and a large, nonmetallic residue remains after treatment with HNO_3 (P. 3), it is sometimes advantageous to analyze the residue separately by the following procedure, by which a large quantity of metastannic acid is more readily dissolved: Add to the residue in a casserole 3–4 ccm. concentrated H_2SO_4, and heat under the hood until the acid has evaporated to a volume of about 2 ccm. Cool, add an equal volume of water, cool again, add 5 ccm. HCl (1.12) to dissolve antimonic oxide, and heat to boiling. Cool completely, filter if there is a residue (which may consist of silicic or tungstic acid), and add the acid solution drop by drop, with constant shaking, to a mixture of 10 ccm. ammonium monosulphide, 1 ccm. ammonium polysulphide, and 10 ccm. NH_4OH (0.90) in a flask. Cover the flask and digest for a few minutes on a steam bath. Filter out the precipitate, which may consist of titanium hydroxide or small quantities of sulphides of the copper and iron groups. Dilute the filtrate, and make it slightly acid with HCl. Shake to coagulate the precipitate,

filter, and wash with hot water. Analyze the precipitate for the tin group by P. 42; reject the filtrate or test it for phosphate with molybdic acid.

Procedure 5.[1] — Transfer to a platinum crucible the residue after treatment with acids (P. 2 or P. 4), add 2 ccm. H_2SO_4 (1.84) from a graduate, heat with a moving flame until white fumes are given off, and cool completely. To test for silica, add carefully (see N. 1), from the loop of a platinum wire, pure 40% HF drop by drop until 5–6 drops have been added, and warm the mixture over a steam bath. (Formation of gas bubbles, presence of SILICA.)

Then add about 5 ccm. more pure 40% HF, cover the crucible with a platinum cover, digest on a steam bath for about 15 minutes unless the residue dissolves more quickly; remove the cover and evaporate carefully until white fumes of H_2SO_4 are given off, heating the sides of the crucible with a moving flame, or, better, with a ring-burner to avoid spattering. [Unless it is known from the presence of solid substance at this point or from previous observations that the residue treated with H_2SO_4 and HF contained other constituents than silica, determine this by evaporating off the H_2SO_4 under a hood, taking care not to ignite the residue. If a significant residue remains, add from a graduate 1.5 ccm. H_2SO_4 (1.84), and heat until the residue is redissolved, not allowing the acid to evaporate.] Cool, pour the contents of the crucible into 10 ccm. water, and rinse out the contents with a little water. Boil to dissolve slowly dissolving sulphates; cool, shake, filter, and wash the residue, first with H_2SO_4 (1.20) and then with a little water, rejecting the washings. (Residue, P. 6.) To the filtrate add HCl drop by drop only as long as a precipitate forms; filter, wash the precipitate, and test it for silver by P. 15. Dilute the filtrate to a volume of 40 ccm., treat it with H_2S by P. 21, subsequently testing for all the metallic elements except lead, barium, and strontium.

Notes. — 1. Great care must be taken not to breathe the fumes of HF nor to get it on the hands; for it is very irritating and produces dangerous burns.

2. The test for silica or silicate depends on the formation of SiF_4 gas, which is insoluble in strong H_2SO_4, but dissolves in water in the presence of HF with formation of fluosilicic acid, H_2SiF_6. With free silica the evolution of gas takes place in the cold; but with slowly decompos-

[1] For an alternative procedure, see N. 7 below and P. 8.

ing silicates, such as feldspar, the test is obtained only upon warming. A few silicates are not acted upon by HF and H_2SO_4, and, of course, do not show the test for silica at this point. The test is delicate enough to enable 1 mgm. of silica, whether free or in a decomposable silicate, to be detected. Moreover, after the substance has been treated with acids as in P. 4 and warmed with H_2SO_4, an evolution of gas with HF is not produced with the compounds of any element other than silicon (not even with those of titanium, niobium, and tantalum, which form somewhat volatile fluorides). It should be borne in mind that a small quantity of silica will be introduced if ordinary filters (which have not been washed with HF) have been employed and have been destroyed by acids or by ignition, or if á strongly alkaline solution has been boiled in glass vessels, or if a substance has been fused with sodium carbonate in a porcelain crucible.

3. Since glass and porcelain consist of silicates which are readily attacked by HF, this acid must not be allowed to come into contact with these materials. In handling cold HF solutions, vessels and funnels of celluloid or paraffin or of glass coated with paraffin may be used; but platinum vessels must be employed when the solutions are to be heated. Care must be taken not to introduce into a platinum vessel any solution containing chlorine or bromine or any acid mixture containing nitrates and chlorides by which chlorine would be evolved. Platinum is so slowly attacked by hot concentrated H_2SO_4 that even when 2–3 ccm. of the acid are rapidly evaporated in a crucible less than half a milligram passes into solution; but, if the acid is boiled for 10–15 minutes in a covered vessel, 2 or 3 mgm. may be dissolved, and would be precipitated subsequently by H_2S.

4. The digestion with HF decomposes most silicates and dissolves silica (and much titanium oxide). The subsequent evaporation with H_2SO_4 expels the excess of HF and decomposes the fluorides produced, as well as some other substances that may have been left undissolved by the HNO_3 and HCl. The H_2SO_4 solution is diluted with a small quantity of water so as to cause the complete precipitation of $BaSO_4$, $SrSO_4$, and $PbSO_4$. These sulphates are moderately soluble in strong H_2SO_4 and may not appear till after dilution. The addition of much water is avoided, since $SrSO_4$ and $PbSO_4$ are somewhat soluble in water; and the residue is washed with dilute H_2SO_4 for the same reason. The solution is boiled so as to dissolve anhydrous sulphates, such as those of aluminum and iron.

5. The residue insoluble in dilute H_2SO_4 contains as sulphates all the barium, strontium, and lead, and all of the calcium in excess of 5–10 mgm., left undissolved by HNO_3 and HCl; more or less of the

chromium (according as the H_2SO_4 has been more or less strongly heated) as a pink anhydrous sulphate; and part of the bismuth as basic sulphate and antimony as antimonic hydroxide, when much of these elements were left undissolved by the previous treatments with acids. The residue may also contain still undecomposed substances, especially the following: silver chloride; corundum, Al_2O_3; chromite, $FeCr_2O_4$; cassiterite, SnO_2; rutile, TiO_2; tungstic oxide, WO_3; molybdenum sulphide, MoS_2; some anhydrous silicates and fluosilicates, such as cyanite or andalusite (Al_2SiO_5) and tourmaline; graphite and carbides.

6. If the presence of silver is shown by the addition of HCl, the residue insoluble in dilute H_2SO_4 is likely to still contain AgCl, which is only slowly decomposed by hot concentrated H_2SO_4. In order to dissolve this, add to the residue in a small casserole 3–5 ccm. concentrated H_2SO_4, heat until white fumes are given off, cover the dish with a large watch glass, and boil gently for 5–10 minutes. Cool, and treat as described in the last paragraph of the above procedure. If AgCl is not completely removed in this way, its presence will be shown by a blackening of the residue upon boiling with Na_2CO_3 solution in P. 6; in such a case it must be removed by further treatment with H_2SO_4 before a fusion with Na_2CO_3 is made in a platinum crucible (P. 7). By this treatment with boiling H_2SO_4, Al_2O_3 and TiO_2, if present in the residue, are also dissolved in large quantity.

7. If the use of a platinum crucible or of hydrofluoric acid is impracticable, the residue insoluble in HCl and HNO_3 may be fused in a porcelain crucible with a mixture of Na_2CO_3 and K_2CO_3, as described in P. 8, instead of being treated by P. 5–7. This is, however, a far less satisfactory method of analysis for the following reasons. Compounds of the alkali elements are used as a flux, and aluminum, calcium, and silica are introduced from the porcelain crucible, so that these elements cannot be tested for in the insoluble residue. Moreover, the treatment with HF and H_2SO_4 is almost always a shorter process, since when the residue consists only of silica, as is often the case with minerals, no further treatment is necessary, and since in other cases there is often no residue to be boiled with Na_2CO_3 solution (P. 6) and seldom one to be fused with Na_2CO_3 (P. 7). A fusion in a platinum crucible with alkali-metal carbonate would be less objectionable; but this is not possible unless reducible metallic elements are known to be absent in the residue (see P. 7, N. 1).

Procedure 6. — Transfer the residue insoluble in H_2SO_4 (P. 5) to a casserole, add about 25 ccm.[1] saturated Na_2CO_3 solution, cover

[1] See, however, *P. 6*a*, N. 1, if a small quantity of tungsten is to be tested for.

the casserole, and boil gently for 10 minutes. Filter and wash the residue thoroughly. (Filtrate, reject or test for tungsten by *P. 6*a*.) Heat the residue with 5 ccm. HCl (1.12), measured in a graduate, and 10 ccm. water; filter, wash the residue, and treat it by P. 7. Dilute the solution to 40 ccm., and treat it with H_2S by P. 21, subsequently testing it only for lead, bismuth, antimony, chromium, barium, strontium, and calcium.

Notes. — 1. The boiling with Na_2CO_3 converts into carbonates the sulphates of lead, calcium, strontium, and bismuth completely, and at least 80% of the sulphate of barium, even when large quantities of them are present. A second treatment, which should be applied to the residue if there are indications that barium is present, completely decomposes $BaSO_4$. The carbonates dissolve readily in HCl. Anhydrous chromic sulphate, which is left undissolved by dilute H_2SO_4 (P. 5) as a fine pink or gray powder, is slowly changed by boiling with Na_2CO_3 to a greenish blue hydroxide which dissolves in the HCl, leaving behind the still undecomposed sulphate. Antimonic oxide dissolves only to a small extent (2–4 mgm.) in the Na_2CO_3 solution, but dissolves upon boiling with HCl. Tungstic oxide passes into the Na_2CO_3 solution as sodium tungstate (Na_2WO_4).

2. Any residue insoluble in HCl can therefore consist only of barium and chromic sulphates or of some of the original substance still undecomposed, consisting, probably, of one of the native oxides or silicates mentioned in P. 5, N. 5. Such a residue will seldom be obtained; and if so, it can ordinarily be rendered soluble by fusion with Na_2CO_3 and KNO_3 (or with KOH) as described in P. 7 (or P. 7, N. 2).

3. The residue undissolved by dilute H_2SO_4 after the treatment with HF (P. 5) is first boiled with Na_2CO_3 solution and not at once fused, since it is necessary to remove the reducible metals, lead, bismuth, and antimony, before a platinum crucible can be used for the fusion. Moreover, the boiling with Na_2CO_3 solution makes subsequent fusion unnecessary when the residue consists only of sulphate of lead or of an alkaline-earth element.

* **Procedure 6a.** — Acidify the Na_2CO_3 solution (P. 6) with HNO_3, evaporate almost to dryness, add 1–2 ccm. HNO_3 (1.20); add enough water to dissolve the salt, boil, and cool. (Yellow precipitate, presence of TUNGSTEN.) Filter and wash the precipitate, rejecting the solution. Pour through the filter 2 ccm. NH_4OH (0.96) to dissolve any H_2WO_4,

acidify the filtrate with HCl (1.20), and add a few granules of zinc. (Blue color, presence of TUNGSTEN.)

Notes. — 1. When HNO_3 is added to a tungstate solution a hydrated tungstic acid separates as a white flocculent precipitate, which changes upon boiling to a yellow powder (H_2WO_4). The test is not very delicate in the presence of a large amount of salt; when 25 ccm. Na_2CO_3 solution are used, as is directed in P. 6, even 3 mgm. of tungsten can barely be detected in this way. Therefore, when tungsten is to be tested for, the residue from P. 5 should first be boiled with a small portion (5 ccm.) of Na_2CO_3 solution, and this solution tested for tungsten as described above; under these conditions 1 mgm. can be detected. The test is entirely unsatisfactory if H_2SO_4 or HCl is used, in place of HNO_3, in neutralizing the Na_2CO_3.

2. The blue color obtained upon reduction with zinc, which serves as a confirmatory test for tungsten, is due to a suspended, quickly coagulating precipitate, consisting of a hydrated oxide intermediate between WO_3 and WO_2. Prolonged action of zinc may cause the blue color to disappear, owing to complete reduction to WO_2.

3. At this point will usually be found all the tungsten in the substance in excess of 2 mgm., which amount remains in solution in the H_2SO_4 (P. 5). When, however, phosphate is also present in the substance, tungsten would not remain as H_2WO_4 in P. 3 and 4, but would pass into the acid solution, owing to the formation of a complex phospho-tungstic acid.

Procedure 7. — Transfer the residue insoluble in HCl (P. 6), with the filter if necessary, to a platinum crucible, heat until the residue is dry or until the filter is destroyed, mix the residue with 5–10 grams of anhydrous Na_2CO_3 and 0.1–0.5 gram of solid KNO_3, cover the crucible, and heat over a powerful burner. After some minutes note whether a perfectly fluid fusion has resulted. If not, heat more intensely over a blast lamp for 10 minutes, adding, if necessary, more Na_2CO_3. Cool, place the crucible in a casserole, add carefully HCl (1.12) till the solution remains strongly acid, evaporate to dryness, and heat at 120°–130° to render silica insoluble; add from a graduate 4 ccm. HCl (1.12) and 10–20 ccm. water, boil, and filter. Dilute the filtrate to 40 ccm., and treat it with H_2S by P. 21, subsequently testing it for all metallic elements except the alkalies. Test the residue for silica by P. 5 and remove it if present; if a residue still remains, treat it as described in N. 3.

Notes. — 1. Compounds of the elements of the silver, copper, and tin groups that may be reduced to the metal by heating with an alkaline flux must not be heated in platinum. The same is true of sulphur, sulphides, and in the presence of organic matter of phosphates; for all these elements form easily fusible alloys with the platinum, and thus spoil the crucible. If, however, the substance has been treated by the preceding procedures, none of these substances can be present. Moreover, alkaline hydroxides and strongly oxidizing fluxes (such as peroxides and nitrates) must not be fused in platinum, since they attack it fairly rapidly. Therefore, no more nitrate should be added to the Na_2CO_3 fusion than is necessary.

2. In regard to the decomposition of substances in general by fusion with Na_2CO_3, see P. 8, N. 1. Of the substances that may be present in the residue which has been boiled with Na_2CO_3 solution, the silicates are decomposed by fusion with Na_2CO_3 alone. But in order to render chromium compounds (and molybdenum sulphide) soluble, they must be oxidized; and for that purpose a little KNO_3 is added. The native and ignited oxides of tin, aluminum, and titanium are only slowly acted upon by the flux, and remain insoluble with the silica upon the subsequent treatment with acid. $BaSO_4$, if still present, will also remain with the silica; for, though it is converted into $BaCO_3$ and Na_2SO_4 by the fusion, it is formed again when the mass is treated with acid.

3. Any residue insoluble in dilute HCl probably consists, therefore, only of SiO_2, TiO_2, $BaSO_4$, Al_2O_3, and SnO_2. Such a residue is best treated first by P. 5 and 6, to remove SiO_2 and $BaSO_4$, and any residue still remaining may then be treated as follows: Reduce it to a very fine powder, transfer it to a nickel or silver crucible, dry thoroughly, add 5–10 grams pure solid KOH, and fuse the mixture for 10–20 minutes. Cool, extract with about 30 ccm. water, and filter. Neutralize the solution exactly with HCl (1.12). Treat the residue with about 5 ccm. HCl (1.12), filter out any residue of undecomposed substance, and unite the solution with the neutral aqueous extract. Treat the mixture by the regular procedure beginning with P. 21, testing especially for tin, titanium, and aluminum. The native and ignited oxides of aluminum, stannic tin, and titanium, if finely powdered, dissolve rapidly in fused KOH; and the aqueous extract contains the aluminum as aluminate and most of the tin as stannate. The residue undissolved by water may consist of black nickel oxide from the crucible, stannic hydroxide, potassium titanate, and sometimes other hydroxides accompanying the aluminum or tin oxides. All of these dissolve in HCl.

Procedure 8. — If the use of HF (P. 5) is impracticable, transfer the residue insoluble in acids (P. 2 or 4), with the filter if necessary, to

a porcelain crucible, heat until the residue is dry or until the filter is destroyed, mix the residue, which must be very finely divided, with ten to twenty times its weight of a mixture of anhydrous Na_2CO_3 and K_2CO_3, cover the crucible, heat strongly over a powerful burner or over a blast lamp so that complete fusion takes place, and continue the heating for 10–30 minutes. If dark particles of undecomposed substance can still be seen, add gradually in small portions 0.1–0.5 gram of solid KNO_3, and heat strongly for several minutes. Cool, boil the crucible and its contents with water until the fused mass is disintegrated, filter, and wash the residue thoroughly. Warm the residue with HNO_3 (1.20) until action ceases, and filter out any still undecomposed substance (see N. 2 below.) Mix a small part of the HNO_3 solution with a small part of the Na_2CO_3 solution, making the mixture strongly acid with HNO_3, if it is not already so.

If no precipitate forms, mix the remainder of the acid solution with about half the Na_2CO_3 solution, reserving the rest of the Na_2CO_3 solution for the tests for acid radicals. Add about 5 ccm. HCl (1.12) (or more if the solution is still alkaline), and filter. (Precipitate, test for silver and lead, P. 12.) Evaporate the solution to dryness, moisten the residue with HCl, and again evaporate to decompose nitrates. Heat the residue until it is thoroughly dry at 120–130° in a hot closet or by keeping it in motion over a small flame. Add from a graduate 4 ccm. HCl (1.12) and about 20 ccm. water; heat to boiling, filter, reject the residue, and dilute the filtrate to 40 ccm. (Filtrate, P. 21.)

If a precipitate forms on mixing small portions of the HNO_3 solution and the Na_2CO_3 solution, treat these solutions separately as described in the preceding paragraph, uniting the precipitates formed by the same group reagent in the subsequent analysis.

Notes. — 1. Upon fusion with Na_2CO_3 most compounds undergo metathesis, the acid radical of the compound combining with the sodium, and the metallic element with the carbonate radical. The carbonate formed is, however, sometimes decomposed by heat with production of the oxide or of the metal itself. Acid-forming oxides, such as SiO_2, As_2O_5, and less rapidly Al_2O_3, expel CO_2 from the Na_2CO_3 and form sodium salts. Such reactions are illustrated by the following equations:

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$
$$Fe_2SiO_5 + Na_2CO_3 = Na_2SiO_3 + Fe_2O_3 + CO_2.$$
$$4AgCl + 2Na_2CO_3 = 4NaCl + 4Ag + 2CO_2 + O_2.$$
$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2.$$

After the treatment with water, the acid radical of the substance is therefore found with the excess of Na_2CO_3 in the aqueous extract, while the metallic component remains undissolved by the water and passes into the acid solution.

2. Some substances which are not much acted upon by Na_2CO_3 alone are readily attacked when an oxidizing flux like KNO_3 is present. Thus sulphides are converted into sulphates and chromium compounds (such as chromite, $FeO.Cr_2O_3$) into chromates. A few substances, however, such as the oxides of tin, aluminum, and titanium, may be only partially decomposed even by long-continued fusion with the mixed fluxes. An undecomposed residue is best fused with KOH in a nickel or silver crucible and the fusion treated, as described in P. 7, N. 3, first with water and then with HCl.

3. The porcelain crucible is so attacked by the flux that it cannot well be used for a second fusion. Aluminum, calcium, and silica are taken up by the flux, so that these elements, as well as the alkali elements, cannot be tested for later in the analysis. In case all reducible metallic elements and sulphides are known to be absent (see P. 7, N. 1), it is therefore better to make the fusion in a platinum crucible, since then no foreign substances are introduced from the crucible. If platinum is not available, or if it is not known that reducible elements are absent, a pure nickel crucible can be used with advantage in place of the porcelain one. This enables aluminum, calcium, and silica to be tested for; some nickel, but only a few milligrams, will then be found in the acid solution of the fusion. Reducible elements, if present, would alloy with the nickel, but the destruction of a crucible of this cheap material is not of much consequence. Ordinarily a nickel crucible can be used repeatedly.

4. The first and third reactions given in N. 1 are examples of cases where the aqueous and acid solutions must not be mixed, for upon mixing $BaSO_4$ or AgCl would again be formed.

5. Of the metallic elements that may be present, all or a part of the arsenic, antimony, tin, molybdenum, tungsten, aluminum, chromium, and manganese are contained in the Na_2CO_3 solution; and this solution must therefore be analyzed for metallic elements. Since this solution may also contain Na_2SiO_3, the solution after the addition of HCl is evaporated to dryness, and the residue is heated at 120–130°; this treatment partially dehydrates the silicic acid and renders it insoluble in HCl. The residue insoluble in HCl after this treatment usually consists only of silicic acid (or tungstic acid). To prove whether it consists wholly of silica, it may be treated with H_2SO_4 and HF as described in P. 5. *To test for tungsten it may be treated with HCl and zinc as described in *P. 6*a*.

6. The residue left after the extraction with water is treated with HNO_3 rather than with HCl, so as to dissolve reduced metals and to prevent the formation of AgCl and $PbCl_2$ at this point.

Confirmatory Experiments and References

P. 2, N. 1: Destruction of Organic Matter. — 3 grams white flour, 1.5 grams glycerin, 0.5 gram paraffin, and some filter paper were treated in separate experiments, according to the procedure: nearly all the organic matter was decomposed by the first two or three treatments with H_2SO_4 and HNO_3, and after a few more treatments colorless solutions were obtained.

P. 2, N. 2. — See C. E., P. 5, N. 4 and 5.

P. 3, N. 7: Oxidation of Mercurous Salts by HNO_3. — 100 mgm. Hg as $Hg_2(NO_3)_2$ were boiled with a little HNO_3 (1.42) for one minute, the solution was diluted, and HCl added: no precipitate was formed, thus showing that the mercurous salts had been completely oxidized. 100 mgm. Hg as $Hg_2(NO_3)_2$ were boiled for 10 minutes with 25 ccm. HNO_3 (1.04), and HCl was added: a large precipitate of Hg_2Cl_2 resulted, showing that dilute HNO_3 does not oxidize a mercurous salt rapidly.

Volatility of Mercury and Arsenic Compounds. — Separate solutions containing 1 mgm. Hg as $HgCl_2$ in HNO_3, HCl, *aqua regia*, and H_2SO_4 were carefully evaporated just to dryness; the residue was in each case dissolved in a little water, and the solution saturated with H_2S: a precipitate of HgS estimated by comparison at not less than $\frac{2}{3}$ mgm. Hg was obtained in each case, showing that not much of the mercury had been volatilized. It was found that $HgCl_2$ was not converted into $Hg(NO_3)_2$ by the evaporation with HNO_3.

1 mgm. Hg as $HgCl_2$ was heated in a hot closet at 125°, the casserole was washed out with water, and the solution saturated with H_2S: no precipitate was obtained, thus showing that the $HgCl_2$ was completely volatilized.

1 mgm. Hg as $Hg(NO_3)_2$ was heated for two days at 125° in a hot closet, dissolved in water, and treated with H_2S: an HgS precipitate resulted, whose size indicated that little or none had volatilized.

10 mgm. As as As_2O_3 were added to 10 ccm. HCl (1.20), and the solution was boiled vigorously for about 15 seconds; the solution was somewhat diluted and then saturated with H_2S: only 1–2 mgm. As as As_2S_3 were precipitated.

The experiment was repeated, except that the HCl solution was evaporated to 2 ccm.: scarcely any precipitate of As_2S_3 was obtained. In another experiment the solution was evaporated to dryness: no precipitate of As_2S_3 formed.

A solution of 10 mgm. As as As_2O_3 in 10 ccm. H_2O and 2 ccm. HCl

After the treatment with water, the acid radical of the substance is therefore found with the excess of Na_2CO_3 in the aqueous extract, while the metallic component remains undissolved by the water and passes into the acid solution.

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6. The residue left after the extraction with water is treated with HNO_3 rather than with HCl, so as to dissolve reduced metals and to prevent the formation of AgCl and $PbCl_2$ at this point.

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10 mgm. As as As_2O_3 were added to 10 ccm. HCl (1.20), and the solution was boiled vigorously for about 15 seconds; the solution was somewhat diluted and then saturated with H_2S: only 1–2 mgm. As as As_2S_3 were precipitated.

The experiment was repeated, except that the HCl solution was evaporated to 2 ccm.: scarcely any precipitate of As_2S_3 was obtained. In another experiment the solution was evaporated to dryness: no precipitate of As_2S_3 formed.

A solution of 10 mgm. As as As_2O_3 in 10 ccm. H_2O and 2 ccm. HCl

(1.20) was boiled for 30 seconds and H_2S was passed in: a precipitate appearing like that given directly by 10 mgm. As was obtained, showing that very little if any arsenic was volatilized. A similar solution of 10 mgm. As was evaporated to 2 ccm.: it gave with H_2S a precipitate estimated to contain 3 mgm. As.

1 and 10 mgm. As as As_2O_3 dissolved in 5–10 ccm. HCl (1.20) were boiled in covered casseroles, oxidized with bromine water, evaporated to dryness, and dissolved in HCl; the solution was then precipitated with H_2S: the amount of arsenic precipitated was estimated to be nearly as great as that originally taken, thus showing that arsenic in the higher state of oxidation is not volatilized.

P. 3, N. 9–12: Solubility of the Dehydrated Hydroxides in HNO_3. — For this and for a statement as to other substances that the residue may contain, see A. A. Noyes, this QUARTERLY, **16**, pp. 121–126 (1903).

P. 4, N. 1: Solubility of $PbSO_4$, $BaSO_4$, AgCl, and $Sn(PO_4)_4$ in HCl. — See this QUARTERLY, **16**, p. 126 (1903).

Action of HCl and HNO_3 on AgCN and AgI. — 50 mgm. Ag as freshly precipitated AgCN were boiled with 20–30 ccm. HCl (1.20): the precipitate dissolved quickly.

To 50 mgm. Ag as freshly precipitated AgI were added 10 ccm. HNO_3 (1.42), and the mixture was evaporated, diluted, filtered, and HCl was added to the filtrate: a precipitate of AgCl estimated to contain 15 mgm. Ag was obtained, showing that AgI is slowly decomposed by HNO_3. The experiment was repeated with 50 mgm. Ag as AgCN: no precipitate of AgCl was obtained.

P. 4, N. 4: Solubility of Metastannic and Antimonic Acids in H_2SO_4 and HCl. — 200 and 400 mgm. Sn as metastannic acid, which had been heated for 1 hour in a hot closet at 120°, were treated in separate experiments with 3 ccm. concentrated H_2SO_4 as described in the Note: in the first case all the tin, in the second all but a few milligrams of it, dissolved on boiling the acid for about a minute. The solutions were diluted with 2–3 ccm. water and boiled: no precipitate formed. The first solution was cooled and poured into 10 ccm. cold water: a solution which remained clear for several hours was obtained, from which a white precipitate separated at once on boiling. To the other solution (containing 400 mgm. Sn) were added 5 ccm. HCl (1.12) and 50 ccm. water: no precipitate appeared, even on boiling. The solution was diluted to 200 ccm.: a white precipitate then formed. The precipitates obtained from these solutions dissolved readily in dilute HCl and in concentrated H_2SO_4.

200 mgm. Sb as hydrated Sb_2O_5, previously heated at 120°, were boiled with 5 ccm. HCl (1.12) for 2 or 3 minutes: complete solution resulted.

200 mgm. Sb as hydrated Sb_2O_5 did not dissolve in 3 ccm. boiling con-

centrated H_2SO_4 or on dilution, but dissolved readily when HCl was added as described in the Note. This solution was diluted with 10 ccm. water: a slight precipitate formed, which dissolved on the addition of a little HCl and warming.

In another experiment 200 mgm. Sn as dehydrated metastannic acid were boiled for about 30 minutes with HCl (1.20): at the end of that time the solid had dissolved nearly, but not quite completely.

Solubility of Metastannic, Antimonic, and Silicic Acids in Ammonium Sulphide. — 200 mgm. metallic antimony and 300 mgm. metallic tin were treated in separate experiments by P. 3 and the procedure described in Note 4: clear solutions were obtained on adding the acid solution to the alkaline ammonium sulphide solution.

The following experiments show that the residue from P. 3 may be treated directly with ammonium sulphide, but that this process is ordinarily a longer one than that described in the Note.

200 mgm. Sn as dehydrated metastannic acid, previously heated at 120°, were warmed gently with successive 10 ccm. portions of the ammonium polysulphide reagent in a covered casserole for 5–10 minutes, with frequent stirring: in the first treatment considerably more than half of the tin dissolved; after the second treatment only about 20 mgm. were left undissolved; and two more treatments dissolved this completely. — The experiment was repeated, using colorless ammonium monosulphide in place of the yellow polysulphide: the same results were obtained.

500 mgm. Sn as dehydrated metastannic acid were treated with successive 10 ccm. portions of yellow ammonium sulphide in a pressure bottle at 70–80°: practically all dissolved in two 10-minute treatments.

200 mgm. Sn as dehydrated metastannic acid dissolved in 10 ccm. ammonium monosulphide in a pressure bottle at 80° in about 10 minutes, and another portion of about 100 mgm. Sn dissolved in the same solution on further heating.

200 mgm. Sb as hydrated Sb_2O_5, previously heated at 120°, were treated in a covered casserole with ammonium polysulphide; it dissolved only very slowly, and several treatments were necessary to effect complete solution. As with metastannic acid, the use of the pressure bottle hastened the solution, but antimonic acid dissolved even less readily than metastannic acid.

100 mgm. dehydrated silicic acid were warmed for 15 minutes with 20 ccm. ammonium monosulphide; the filtrate was acidified, evaporated to dryness, and tested for silica by P. 5: very little, if any, gas evolution was obtained, thus showing that SiO_2 is insoluble in ammonium sulphide. — In another experiment only a few milligrams (1–3) SiO_2 dissolved in 30 ccm. boiling ammonia (0.96) in 15 minutes.

P. 5, N. 2: The Test for SiO_2 with HF and H_2SO_4. — 1 and 2 mgm. of

dehydrated H_2SiO_3 were treated as described in the first paragraph of P. 5: evolution of gas took place at room temperature and was easily seen in both cases.

1 and 2 mgm. SiO_2 as feldspar, which had been well purified from free silica by long-continued boiling with Na_2CO_3 solution, were treated in separate experiments according to P. 5: there was no evolution of gas in the cold, but a distinct one took place on warming.

500 mgm. $BaSO_4$, 100 mgm. TiO_2, 100 mgm. tantalic acid, and 150 mgm. niobic acid were treated by P. 5: no evolution of gas was observed in the cold nor on warming, provided the solid had been previously heated with the strong H_2SO_4 to remove air bubbles.

A filter (Schleicher und Schüll, No. 597) 11 cm. in diameter, with an ash stated to be 0.0028 gram, was treated by P. 2, to destroy organic matter, and the residue by P. 5, to test for silica: bubbles of gas were clearly seen.

In a series of experiments an attempt was made to test for silica by adding HF to the dry solid and allowing the SiF_4 evolved to act on a drop of water held in the loop of a platinum wire near the solid. The best conditions were found to be to add less HF than corresponded to the silica present, to allow the reaction to continue until almost all the HF was destroyed, the action being accelerated by stirring with a heavy platinum wire, and then to warm the mixture gently, while holding the drop of water near the solid. Even under these conditions, however, the drop did not become turbid when less than 5 mgm. SiO_2 were used, although an evolution of gas doubtless took place, as was shown by a hissing sound.

P. 5, N. 3: Action of Hot H_2SO_4 on Platinum. — 5 ccm. H_2SO_4 (1.84) were evaporated to 2 ccm. in an open platinum crucible within 2 or 3 minutes, cooled, diluted with 5–10 ccm. water, and H_2S passed into the hot solution for some minutes: a brown coloration appeared quickly, but no precipitate settled out.

5 ccm. H_2SO_4 (1.84) were boiled for 15 minutes in a covered platinum dish previously weighed, cooled, diluted, and saturated hot with H_2S: a precipitate of PtS_2 estimated to contain 2–3 mgm. Pt was obtained and the dish had lost 3 mgm. in weight.

P. 5, N. 4: Action of H_2SO_4 and HF on Minerals and Other Substances. — Each of the following substances was treated with the stated result by the following procedure, which is similar to the regular process, P. 4–6, except that in these experiments the substance was digested for a longer time with hot concentrated H_2SO_4. 1 gram was digested for several minutes in a covered platinum dish with 10 ccm. HNO_3 (1.42). 3 ccm. H_2SO_4 (1.84) were then added, the mixture was evaporated to distinct fuming, and maintained at that point for 10 minutes. 5 ccm. HF were added, the mixture was digested for 15 minutes on a water bath, and then evaporated until

thick acid fumes were given off; 3 ccm. HF were added, and the mixture was again evaporated to fuming. 30 ccm. water were added, the mixture was boiled for 15 minutes, cooled, diluted to 100 ccm., and the residue washed once by decantation. 30 ccm. saturated Na_2CO_3 solution were then poured over the residue, and the mixture was allowed to stand, with frequent stirring, for 15 minutes. The solution was decanted, and the residue washed twice with water, after which it was treated with 30 ccm. HCl (1.02). A large residue was left after the final treatment with HCl by cassiterite (SnO_2), emery (Al_2O_3), chromite ($FeO.Cr_2O_3$), rutile (TiO_2), cinnabar (HgS), molybdenite (MoS_2), tourmaline, beryl ($Be_3Al_2Si_6O_{18}$), and columbite ($Fe(Nb,Ta)_2O_6$). About a third of the molybdenite was decomposed by the HNO_3 with separation of some molybdic acid, which dissolved in the H_2SO_4. Cinnabar, rutile, and beryl were much attacked by H_2SO_4, and columbite by HF, but the other substances were attacked not at all, or only very slightly, by any of the reagents. — Fluorspar (CaF_2), chrome yellow ($PbCrO_4$), wulfenite ($PbMoO_4$), and vanadinite ($3Pb_3V_2O_8.PbCl_2$) were attacked by HNO_3 and by H_2SO_4; titanite ($CaTiSiO_5$), garnet ((Ca, Mg, Mn,Fe)$_3Al_2Si_3O_{12}$), a cement, and some slags containing lead or calcium, were attacked by these acids and also by HF. All left, after the treatment with HF and H_2SO_4, a white residue, which, after the treatment with Na_2CO_3, dissolved completely in HCl. The white residue, therefore, contained only insoluble sulphates, such as $PbSO_4$, $CaSO_4$; and the substances were completely decomposed by the treatment with HNO_3, H_2SO_4, and HF. — Wolframite ((Fe, Mn)WO_4), menaccanite ($FeTiO_3.Fe_2O_3$), and Prussian blue were decomposed by H_2SO_4, and all left a residue insoluble in dilute H_2SO_4, which dissolved completely, or nearly so, in Na_2CO_3. — Magnetite (Fe_3O_4), cryolite (Na_3AlF_6), basalt, granite, monazite, a uranium ore, and a number of slags were completely decomposed after the treatment with HNO_3, H_2SO_4, and HF, and dissolved completely in the dilute H_2SO_4.

For the action of HF and HNO_3 on some other difficultly soluble native silicates, see this QUARTERLY, **16**, p. 126 (1903).

P. 5, N. 4 and 5: Solubility of Sulphates in Concentrated and Dilute H_2SO_4. — 100 mgm. and 150 mgm. Ba as $BaSO_4$ were strongly heated with 2 ccm. concentrated H_2SO_4: a clear solution resulted in the first case, but not in the second. $BaSO_4$ was precipitated at once when a little water was added.

For the solution of $PbSO_4$ in concentrated H_2SO_4, see C. E. on P. 26, N. 1.

10, 15, and 20 mgm. Ca as $Ca(NO_3)_2$ were added in separate experiments to 20 ccm. H_2SO_4 (1.20): with the 20 mgm. a precipitate separated at once and with the 15 mgm. after about 5 minutes, while with the 10 mgm. none formed, even after several hours.

300 mgm. Al, 300 mgm. Fe, 100 mgm. mercuric Hg, and 150 mgm. Cu,

all as sulphates, were in separate experiments boiled with concentrated H_2SO_4, cooled, diluted, and again boiled as described in the procedure: the anhydrous $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ dissolved completely after about 3 minutes' boiling; the anhydrous $CuSO_4$ and the $HgSO_4$ dissolved at once on warming.

To 100 mgm. Cr as $Cr_2(SO_4)_3$ in solution as green sulphate 2 ccm. H_2SO_4 (1.84) were added, and the solution was evaporated until thick acid fumes came off; the mixture was cooled, diluted, and boiled, the whole treatment being as in the Procedure: the resulting solution was green, and from its color was estimated to contain 10–15 mgm. Cr; the remainder of the chromium was left as a very finely divided light-pink powder (anhydrous $Cr_2(SO_4)_3$). — This experiment was repeated, except that the H_2SO_4 was heated only until slight fumes appeared: no pink precipitate separated, and on boiling with water a clear green solution was obtained.

100 and 200 mgm. Cr as precipitated $Cr(OH)_3$ were dissolved in 5 ccm. H_2SO_4 (1.84) and 20 ccm. water; the solutions were evaporated to about 2 ccm., cooled, diluted, again boiled, and filtered: a very finely divided, gray to pink powder (anhydrous $Cr_2(SO_4)_3$) was obtained, which ran through the filter. The precipitate was allowed to settle and the solution was decanted and boiled with NH_4OH: it was colorless and gave scarcely any precipitate of $Cr(OH)_3$. The anhydrous sulphate was boiled for 15 minutes with dilute H_2SO_4: only a few milligrams dissolved. The sulphate was found to be slowly dissolved by a concentrated Na_2O_2 solution owing to oxidation to chromate.

500 mgm. Sb as $SbCl_3$, 50 mgm. antimonic Sb ($SbCl_3$ previously boiled with HNO_3 and HCl), and 500 mgm. Bi as $Bi(OH)_3$ were heated in separate experiments with 3–5 ccm. H_2SO_4 (1.84), evaporated to 2 ccm., diluted to about 20 ccm., and again boiled. With the antimonous salt a crystalline precipitate was obtained on evaporating the H_2SO_4 solution; this precipitate dissolved when the 20 ccm. water were added, but an amorphous precipitate formed when much more water was added. The antimonic antimony was precipitated in the concentrated H_2SO_4 as an amorphous powder, and more of this precipitate separated on dilution; the dilute H_2SO_4 solution was filtered and the amount of antimony contained in the filtrate was estimated by precipitating with H_2S to be about 10 mgm.; the residue insoluble in H_2SO_4 was washed with water and dissolved in boiling HCl, and to the solution $BaCl_2$ was added: only a slight precipitate of $BaSO_4$ was formed, showing that the residue was an oxide or hydroxide, not a sulphate. In the experiment with bismuth the hydroxide dissolved in H_2SO_4, and a crystalline precipitate (sulphate) separated from the hot concentrated H_2SO_4, but the larger part of this dissolved on adding the water, provided the solution was kept cold; a precipitate (of oxysulphate)

appeared when this solution was heated; the filtrate from this was treated with NH_4OH, and a precipitate was obtained which was estimated to contain 20–50 mgm. Bi.

P. 5, N. 6: Decomposition of Silver Salts by H_2SO_4. — 500 mgm. Ag as precipitated AgCl, 500 mgm. Ag as fused AgCl, 100 mgm. Ag as precipitated AgCN, and 100 mgm. Ag as precipitated AgI were treated with H_2SO_4 as described in P. 5: there was a residue in each case. HCl was added to the H_2SO_4 solution: a small precipitate of AgCl was then obtained, showing that some of the silver salt had been decomposed. The residues were boiled with 5 ccm. H_2SO_4 (1.84) in a covered casserole for several minutes: AgI and AgCN dissolved readily in less than 5 minutes, and almost all the AgCl in less than 10 minutes.

500 mgm. Ag as AgCl were boiled with Na_2CO_3 solution (as described in P. 6) for 15 minutes: the AgCl precipitate quickly turned black. The Na_2CO_3 solution was acidified with HNO_3, and $AgNO_3$ added: a precipitate of AgCl, estimated to contain 2 mgm. Ag, formed, showing that only this amount of Ag as AgCl had been converted into silver oxide.

Action of H_2SO_4 on Al_2O_3 and TiO_2. — 2 grams coarsely powdered corundum, which had been previously digested with HF, and 0.5 gram rutile were in separate experiments boiled with 10 ccm. H_2SO_4 (1.84) in a covered casserole for 15 minutes; the mixture was diluted, filtered, and the filtrate made alkaline with NH_4OH: about 50 mgm. Al and about half the titanium were precipitated as hydroxides.

100 mgm. Al as Al_2O_3, obtained by igniting $Al(OH)_3$, were boiled with 5 ccm. H_2SO_4 (1.84) in a covered casserole for 10 minutes: a residue containing 10–20 mgm. Al was left undissolved, and this did not dissolve completely on two more treatments with H_2SO_4. — The experiment was repeated with 200 mgm. Ti as ignited TiO_2: nearly all of it dissolved in 3–4 minutes.

P. 6, N. 1: Action of Boiling Sodium Carbonate Solution on $BaSO_4$, $Cr_2(SO_4)_3$, and Sb_2O_5. — 500 mgm. Ba as $BaSO_4$ were treated by the procedure: a residue of $BaSO_4$ corresponding to about 30 mgm. Ba remained on adding HCl. This residue was treated a second time by the procedure: not more than 1–2 mgm. Ba as $BaSO_4$ then remained.

100 and 200 mgm. Cr as anhydrous $Cr_2(SO_4)_3$, obtained as described under C. E., P. 5, N. 4 and 5, were boiled with Na_2CO_3 in a covered casserole as described in P. 6: the pink precipitate slowly became greenish blue in color. The Na_2CO_3 solution was acidified with HCl, and $BaCl_2$ added to it: a precipitate of $BaSO_4$ was formed, thus showing that chromic sulphate was being decomposed.

The greenish blue residue from the experiment with 100 mgm. Cr (which in contrast to the anhydrous sulphate filtered easily) was boiled with HCl:

some chromium dissolved, but the greater part was left as undecomposed anhydrous sulphate.

The greenish blue residue from the experiment with 200 mgm. Cr was boiled for about 2 hours with seven successive portions of Na_2CO_3 solution, and these solutions were tested for sulphate. The sulphate in these portions steadily decreased in amount and the last portion was free from it. The greenish blue residue now dissolved completely in HCl on warming, and the solution gave no precipitate with $BaCl_2$, showing that the chromic sulphate had been completely converted into the hydroxide.

100 mgm. Sb as antimonic hydroxide, obtained as described under C. E., P. 5, N. 4 and 5, were boiled with 25 ccm. Na_2CO_3 solution in a covered casserole for 15 minutes; the solution was acidified, and treated with H_2S: an orange precipitate of sulphide was obtained which was estimated to contain 3–4 mgm. Sb.

**P. 6a, N. 1: Precipitation of H_2WO_4 from Na_2CO_3 Solution by Acids.* — 1 mgm. W as Na_2WO_4 was added in separate experiments to 5 ccm. H_2O, to 5 ccm. saturated Na_2CO_3 solution, and to 20 ccm. Na_2CO_3 solution; HNO_3 was added in excess and the solutions evaporated almost to dryness: yellow H_2WO_4 separated in the presence of HNO_3 alone, but not in the solutions containing $NaNO_3$. The latter were diluted with enough hot water to dissolve the salt, 1–2 ccm. HNO_3 (1.20) were added, the solutions were boiled vigorously and then cooled: yellow H_2WO_4 precipitated in the solution containing the smaller amount of salt, but not in the other solution. — The experiment with 20 ccm. Na_2CO_3 solution was repeated except that 2 mgm. and 3 mgm. W (in separate experiments) were taken: no yellow precipitate was obtained with 2 mgm., and only a slight one with 3 mgm., thus showing that the presence of $NaNO_3$ interferes with the test.

Solutions containing, respectively, 1, 2, 5, 10, and 20 mgm. W as Na_2WO_4 in 20 ccm. Na_2CO_3 solution were evaporated with excess of H_2SO_4 to strong fuming, diluted to about 15 ccm., boiled, and cooled again: no yellow precipitate was formed in any of the experiments. — Solutions containing 2, 3, 5, and 10 mgm. W as Na_2WO_4 in 20 ccm. Na_2CO_3 solution were evaporated with excess of HCl almost to dryness, diluted to about 15 ccm., boiled, and cooled: no yellow precipitate was formed. The final solutions obtained in all these experiments turned blue when some granules of zinc were added, though the color from 1 mgm. W in H_2SO_4 appeared only after several minutes.

P. 6a, N. 2.: Reduction of H_2WO_4 with Zinc.* — See v. d. Pfordten, *Ber. d. chem. Ges.*, **16, 508 (1883).

To 10 mgm. W as Na_2WO_4 in a test tube were added 5 ccm. water, 5 ccm. HCl (1.12), and a few granules of zinc: a white precipitate separated when HCl was added, and a deep blue color resulted from the action of the

zinc; after half an hour the blue color had changed to a dark brown, and a dark-colored precipitate was suspended in the solution.

**P. 6a, N. 3: Solubility of H_2WO_4 in Acids.* — 2 mgm. W as Na_2WO_4 were treated by P. 3, 4, and 5 except that no HF was added: a yellow precipitate of H_2WO_4 was obtained on boiling with HNO_3 and was not dissolved by dilute HNO_3 after the evaporation (P. 3); the residue dissolved in HCl (1.20) on boiling, but H_2WO_4 was reprecipitated on evaporating the *aqua regia* and was not dissolved by the dilute HCl (P. 4). Nearly all the residue dissolved, however, in 2 ccm. H_2SO_4 (1.84) and did not reprecipitate on diluting to 20 ccm. and boiling (P. 5). — For the solubility of H_2WO_4 in concentrated H_2SO_4 and after dilution, see this QUARTERLY, 17, 249 (1904).

P. 7, N. 2: Effect of fusing Al_2O_3, SnO_2, TiO_2, MoS_2 with Na_2CO_3 or with Na_2CO_3 and KNO_3. — For the fact that a large residue remains when native Al_2O_3, TiO_2, and SnO_2 are fused with Na_2CO_3, see this QUARTERLY, 16, 127 (1903).

80 mgm. Al as Al_2O_3, obtained by igniting precipitated AlO_3H_3 over a blast lamp for 15 minutes, were fused with 8 grams Na_2CO_3 in a platinum crucible over a powerful burner for 20 minutes; 0.2 gram KNO_3 was then added and the heating continued for 10 minutes longer; the fusion was cooled and digested with HCl: only a small residue of unattacked Al_2O_3, corresponding to 5–10 mgm. Al, remained. The solution gave no precipitate with H_2S, showing that platinum had not been removed from the crucible.

500 mgm. Mo as molybdenite (MoS_2) were fused for 3–5 minutes in a porcelain crucible with 10 grams Na_2CO_3 and the mass treated with water; the black particles of MoS_2 all dissolved during the fusion, and the mass, which had a light red color, dissolved nearly completely in water. HCl was added to the solution: a large black precipitate separated.

150 mgm. Mo as molybdenite were fused for about 2 minutes in a platinum crucible with 8 grams Na_2CO_3 and 0.5 gram KNO_3, and the mass was treated with dilute HCl: complete solution resulted; the platinum crucible was not injured. — The experiment was repeated except that the KNO_3 was added after a minute's fusion with Na_2CO_3: the result was the same.

P. 7, N. 2 and P. 8, N. 3: Effect of Fusing Al_2O_3, SnO_2, TiO_2 with KOH. — 200 mgm. of coarsely powdered corundum (Al_2O_3) that had been previously digested with HF and with concentrated H_2SO_4 and 200 mgm. of finely powdered cassiterite (SnO_2) were fused with 10 grams KOH in nickel crucibles for 15 minutes; the mass was extracted with water and the residue heated with HCl: a residue still remained, which was estimated to contain about half the Al_2O_3, but little, if any, of the SnO_2. An analysis was made of the aqueous extract and of the HCl solution: the former was found to contain about 50 mgm. Al (as aluminate) and 100–150 mgm. Sn

(as stannate), but no nickel; the HCl solution contained 20–40 mgm. Sn, 10–15 mgm. Ni, and some Fe as chlorides, but no other metallic element.

1 gram of rutile containing 600 mgm. Ti was treated by P. 3, 4, and 5; the residue was fused with KOH for about 5 minutes as described in P. 7, N. 3; the mass was extracted with water, and the residue treated with cold HCl (1.12): the rutile was not attacked by HNO_3 (P. 3) nor by HNO_3 and HCl (P. 4), but about 300 mgm. Ti were dissolved by H_2SO_4 and HF (P. 5); much of the TiO_2 dissolved in the fused KOH, but only 2–3 mgm. Ti passed into solution on treating the mass with water; out of the residue, which consisted of a black and white mixture, about 200 mgm. Ti dissolved on treating with HCl (1.12); and a black residue of unattacked rutile still remained, which weighed 150 mgm., corresponding to about 90 mgm. Ti. This was powdered finely, again fused with KOH for 15 minutes, and extracted with dilute HCl: all but 3–4 mgm. Ti dissolved.

P. 8, N. 3: Foreign Substances Introduced from Porcelain or Nickel Crucibles. — 10 grams of a mixture of K_2CO_3 and Na_2CO_3 were fused in a porcelain crucible for half an hour over a powerful burner, the mass treated as described in the procedure, and the residue and solution analyzed separately: the residue after the evaporation to dryness with HCl was shown by P. 5 to contain several milligrams of SiO_2; the solution was found to contain several milligrams of aluminum and of calcium and a trace of iron. Compare also C. E., P. 8, N. 5 below.

The experiment was repeated, using a nickel crucible: the aqueous extract acidified with HCl gave no precipitate with H_2S nor with NH_4OH and $(NH_4)_2S$. A slight black residue of nickel oxide insoluble in water remained: this dissolved in HCl and gave a precipitate with NH_4OH and $(NH_4)_2S$, which was estimated to contain 1 mgm. Ni. — This experiment was repeated, except that 0.3 mgm. KNO_3 was added to the fusion: 4–5 mgm. Ni as nickel oxide were obtained.

Reduction of Silver and Lead Compounds by Fusion in a Nickel Crucible.— 200 mgm. Ag as precipitated AgCl were fused with 10 grams of a mixture of Na_2CO_3 and K_2CO_3 in a nickel crucible for 10 minutes and the mass extracted with water: a residue of bright-colored metallic silver soluble in HNO_3 was left as a loose mass which did not adhere to the crucible, there being no evidence of the formation of an alloy.

200 mgm. Pb as precipitated $PbSO_4$ were fused as in the preceding experiment: neither the aqueous extract (when acidified with HCl) nor the HCl solution of the residue gave precipitates with H_2S. The lead salt was completely reduced to metallic globules which had melted on to the nickel crucible, and were not dissolved off by fusion with KOH, KOH and KNO_3, KOH and Na_2O_2, or Na_2O_2 alone.

P. 8, N. 5: Behavior of Antimony and Tin Compounds on Fusion with

Sodium Carbonate. — 60 mgm. Sn as $SnCl_2$ and 50 mgm. Sb as $SbCl_3$ were fused in a porcelain crucible with 10 grams of a mixture of K_2CO_3 and Na_2CO_3 for half an hour; the fusion was extracted with water and with HCl as described in the procedure, and the solutions separately analyzed: the aqueous extract contained nearly all the antimony and tin, a few milligrams of silica, aluminum, and a little calcium; the HCl solution contained 4–5 mgm. antimony, and 1–2 mgm. each of aluminum, iron, and calcium.

PART II. ANALYSIS OF THE SILVER, COPPER, AND TIN GROUPS

General Discussion

A survey of the main features of the method adopted for the analysis of the hydrochloric acid and hydrogen sulphide precipitates may be obtained by referring to the "Tabular Outline" following this chapter. Here only the modifications introduced into the process ordinarily followed will be discussed.

In the precipitation and analysis of the silver group the usual process has been adhered to, the only addition being a provision for the detection of thallium by removing the lead with sulphuric acid and then adding potassium iodide.

In the directions for the precipitation of the copper and tin groups by hydrogen sulphide, especial attention is given to securing the proper conditions as to acid concentration and temperature for a satisfactory separation of these elements from those of the iron group; for indefiniteness in this respect is one of the most common sources of difficulty to the inexperienced analyst. In our process, as will be seen by reference to P. 21, it is directed to precipitate first from a hot, moderately acid solution. The fairly large acid concentration has the advantage of preventing the precipitation by hydrolysis of basic salts of titanium, bismuth, and antimonous antimony, and of hastening the precipitation of the arsenic. The high temperature promotes the precipitation of arsenic, molybdenum, and platinum, and causes all the sulphides to separate in a more readily filterable form. The solution is, however, finally diluted so as to contain 4 ccm. of hydrochloric acid of specific gravity 1.12 in 100 ccm., and is saturated with hydrogen sulphide in the cold; for only with an acid as dilute as this and then in the cold is it possible to precipitate as little as 1 or 2 mgm. of cadmium or lead.

Attention may be called to our experiments described in the chapter on "Confirmatory Experiments and References," which show that under these conditions the separation is a remarkably satisfactory one —at any rate from a qualitative analysis point of view, since not only is the precipitation of the copper and tin groups complete, but one milligram of zinc, iron, or nickel is found in the filtrate, even when 500 milligrams of cadmium, copper, or tin are present.

In the case of substances originally dissolved without the use of nitric acid, which may therefore contain tin or antimony in the stannous or antimonous state, the hydrogen sulphide precipitate is, as usual, treated with ammonium polysulphide. The separation of certain elements by this reagent is, however, far from complete. Thus copper and mercury dissolve in not insignificant quantity in the polysulphide; and tin may remain entirely undissolved, even when several milligrams are present, if cadmium, copper, or mercury is also present in large quantity; moreover, gold, platinum, and the elements allied to them divide themselves between the residue and solution to so large an extent and to so different an extent in different combinations, as to make this reagent entirely unsatisfactory for separating these elements; and with molybdenum the solution is seldom complete, though a large proportion of it always dissolves. New experiments confirmatory of these already known facts will be found described below in the chapter on "Confirmatory Experiments." Yet in a scheme devoted primarily to the common elements there seems to be no alternative process of separation which, on the whole, is nearly so satisfactory; especially since it is not difficult to separate tin from the elements of the copper group in the course of the analysis of the latter, and since enough copper and mercury always remain undissolved by the ammonium polysulphide to enable as little as two milligrams to be detected.

In the case of substances not completely soluble in water, the treatment with nitric acid, recommended in Part I, converts tin and antimony into the higher state of oxidation; and this makes it practicable, as our experiments have shown, to substitute ammonium monosulphide for the polysulphide in the case of such substances, which constitute by far the larger proportion of those ordinarily submitted to analysis. This has the advantage of not dissolving cupric and mercuric sulphides appreciably, thereby not only making the tests for copper and mercury more delicate, but also making it possible to decide with certainty from the appearance of the precipitate produced by acid in the ammonium

sulphide solution whether or not any element of the tin group is present. The monosulphide has, of course, the same defects as the polysulphide in not completely extracting tin and the rarer elements, but not in any more marked degree when these elements are in the higher state of oxidation. This will be evident by reference to the "Test Analyses of the Tin Group."

In the process of analysis of the copper group (see Table V) the only important modification introduced has reference to the extraction of the tin, which may, as just stated, remain wholly in the residue undissolved by ammonium sulphide. The residue undissolved by nitric acid, which may consist of mercuric sulphide and metastannic acid, is treated with bromine water instead of with an acid oxidizing mixture, in order to dissolve out the mercury and leave behind the tin, which can then be dissolved in ammonium sulphide and united with the main solution of the tin group.

For the analysis of the tin group various processes have been proposed and are in general use. As will be seen from Table VI, the method of separation here adopted is based entirely on the different solubilities of the three sulphides of arsenic, antimony, and tin in hydrochloric acid of varying concentration. This process, which seems to have been first suggested for the separation of antimony and tin by Loviton (*J. Chem. Soc.*, **54**, 992. 1888), and which has been utilized in part by Bailey and Cady in their text-book on qualitative analysis, we have somewhat developed by a detailed study of the best conditions for making it a good qualitative method. We believe this method is the one best adapted to the purposes of ordinary qualitative analysis, because of its great simplicity, and because of the fact that the tests, while being of sufficient delicacy to detect one milligram of any of these elements, do not have in the case of arsenic and antimony the extreme sensitiveness of the reduction tests based on the decomposition by heat of hydrogen arsenide and antimonide.

Of the rarer elements precipitable by hydrogen sulphide, provision has been incidentally made for the detection of all the more important ones, namely for that of molybdenum, selenium, tellurium, gold, and platinum. The treatment with hot concentrated hydrochloric acid employed for separating the sulphides of antimony and tin from that of arsenic makes such provision comparatively simple; for the sulphides of all these rarer elements are left, with that of arsenic, together at one place in the scheme (except that gold and platinum may also remain

in the copper group residue, and have to be tested for also in the analysis of that group). No attempt has been made to include the other so-called platinum elements, since the reliable detection of these can be effected only by a special and complicated process. These elements will be treated in the "System of Analysis Including Nearly All the Metallic Elements," which is being published in this QUARTERLY.

TABULAR OUTLINE

TABLE IV

ANALYSIS OF THE SILVER GROUP

Precipitate: $AgCl$, Hg_2Cl_2, $PbCl_2$, *TlCl. *Treat with hot water (P. 12).*

<table>
<tr><td colspan="2">Solution: $PbCl_2$, *TlCl.
Add H_2SO_4 (P. 13).</td><td colspan="2">Residue: $AgCl$, Hg_2Cl_2.
Pour NH_4OH through the filter (P. 15).</td></tr>
<tr><td>Filtrate: *Tl_2SO_4.
Add KI (*P. 13a).</td><td rowspan="2">Precipitate: $PbSO_4$.
Dissolve in $NH_4C_2H_3O_2$, add K_2CrO_4 (P. 14).</td><td rowspan="2">Black Residue:
$HgNH_2Cl + Hg$.</td><td>Solution: $Ag(NH_3)_2Cl$.
Add HNO_3 (P. 15).</td></tr>
<tr><td>Yellow precipitate:
*TlI.</td><td>White precipitate:
AgCl.</td></tr>
<tr><td colspan="2"></td><td>Yellow precipitate:
$PbCrO_4$.</td><td colspan="2"></td></tr>
</table>

TABLE V

ANALYSIS OF THE COPPER GROUP

H_2S PRECIPITATE: HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5 (with As_2S_3 and S_2), Sb_2S_3, Sb_2S_5, SnS, SnS_2, *PtS_2, *Au and *Au_2S_{1-3}, *Se, *Te (and TeS_2?), *MoS_{2-3}.
Digest with ammonium sulphide (P. 22).

<table>
<tr><td colspan="7">Residue: HgS, PbS, Bi_2S_3, CuS, CdS, [*PtS_2], [*Au and Au_2S_{1-3}], [*MoS_{2-3}]. Boil with HNO_3 (P. 23).</td><td rowspan="2">Solution: $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$, *$(NH_4)_2PtS_3$ (?), *$(NH_4)_3AuS_3$ (?), *$(NH_4)_2SeS_3$ (?), *$(NH_4)_2TeS_3$ (?), *$(NH_4)_2MoS_4$. Add HCl (P. 41).

Precipitate: See Table VI.</td></tr>
<tr><td colspan="4">Residue: HgS, SnO_2, *Au and *Au_2S_{1-3}, *PtS_2. Add Br_2 solution (P. 24).</td><td colspan="3">Solution: Pb, Bi, Cu, Cd as nitrates. Add H_2SO_4, evaporate, add water (P. 26).</td></tr>
<tr><td rowspan="4">Residue: SnO_2. Dissolve in $(NH_4)_2S$ (P. 25). Unite with tin group (P. 41).</td><td colspan="3">Solution. Add KCl, evaporate to a small volume (*P. 24a).</td><td rowspan="4">White precipitate: $PbSO_4$. Dissolve in ammonium acetate, add K_2CrO_4 (P. 14).</td><td colspan="3">Filtrate. Add NH_4OH (P. 27).</td></tr>
<tr><td rowspan="3">Yellow precipitate: *K_2PtCl_6.</td><td colspan="2">Filtrate. Add NaOH and $H_2C_2O_4$, and heat (*P. 24a).</td><td rowspan="3">Yellow precipitate: $PbCrO_4$.</td><td>Precipitate: $Bi(OH)_3$. Dissolve in HCl, evaporate, add to water (P. 28).</td><td colspan="2" rowspan="2">Filtrate: $Cu(NH_3)_4SO_4$ (blue), $Cd(NH_3)_4SO_4$.</td></tr>
<tr><td>Purple precipitate: *Au.</td><td>Solution. Add $SnCl_2$ (P. 24).</td><td>White precipitate: BiOCl. Add Na_2SnO_2.</td></tr>
<tr><td>White or gray precipitate: Hg_2Cl_2 or Hg.</td><td>Black residue: Bi.</td><td>To a small part add CH_3COOH and $K_4Fe(CN)_6$ (P. 29).</td><td>To the remainder add KCN and H_2S (P. 30).</td></tr>
<tr><td colspan="4"></td><td colspan="2">Red precipitate: $Cu_2Fe(CN)_6$. White precipitate: $Cd_2Fe(CN)_6$.</td><td>Yellow precipitate: CdS.</td></tr>
</table>

TABLE VI

ANALYSIS OF THE TIN GROUP

PRECIPITATE FROM AMMONIUM SULPHIDE SOLUTION: As_2S_5, Sb_2S_5, SnS_2, *PtS_2, *Au_2S_{3-6}, *SeS_2 (?), *TeS_2 (?), *MoS_3. *Heat with 10 ccm. HCl (1.20) (P. 42).*

<table>
<tr><td colspan="3">Solution: $SbCl_3$, $SnCl_4$. Dilute to 50 ccm., heat, and pass in H_2S (P. 45).</td><td colspan="5">Residue: As_2S_5, *PtS_2, *Au, *Se, *Te, *MoS_3. Dissolve in HCl and $KClO_3$, evaporate to a small volume (P. 43).</td></tr>
<tr><td rowspan="3">Orange precipitate: Sb_2S_3. Dissolve in HCl, add Zn and Pt (P. 46).</td><td rowspan="3">Solution: $SnCl_4$. Cool, dilute, pass in H_2S (P. 47.)</td><td rowspan="3">Yellow precipitate: *K_2PtCl_6. Dissolve in hot water, add KI (*P. 43a).</td><td colspan="4">Filtrate: H_3AsO_4, *$AuCl_3$, *H_2SeO_3, *H_2TeO_3, *H_2MoO_4. Add NH_4OH, NH_4Cl, and $MgCl_2$ (P. 44).</td></tr>
<tr><td rowspan="2">White precipitate: $MgNH_4AsO_4$. Dissolve in HCl, add H_2S (P. 44).</td><td colspan="3">Filtrate. Heat with $H_2C_2O_4$, filter (*P. 43b).</td></tr>
<tr><td rowspan="2">Yellow precipitate: As_2S_5, As_2S_3, and S.</td><td rowspan="2">Purple or dark yellow precipitate: *Au.</td><td colspan="3">Filtrate. Evaporate, add strong HCl and Na_2SO_3 (*P. 43c).</td></tr>
<tr><td rowspan="2">Black deposit: Sb. Treat with NaOCl.</td><td rowspan="2">Yellow precipitate: SnS_2. Dissolve in HCl, add Zn (P. 47).</td><td rowspan="2">Dark red color: *K_2PtI_6.</td><td rowspan="2">Red precipitate: *Se.</td><td colspan="2">Filtrate. Add water and KI (*P. 43d).</td></tr>
<tr><td rowspan="2">Black deposit: Sb.</td><td rowspan="2">Gray deposit: Sn. Dissolve in HCl, add $HgCl_2$ (P. 47).</td><td rowspan="2">Black precipitate: *Te.</td><td>Filtrate. Boil off SO_2, add KCNS and Zn (*P. 43e).</td></tr>
<tr><td>Deep red color: *$Mo(CNS)_4$.</td></tr>
<tr><td></td><td>White precipitate: Hg_2Cl_2.</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

Procedures and Notes

Analysis of the Silver Group

Procedure 11. — To the cold aqueous solution of the substance (P. 3) add 4 ccm. HCl (1.12) from a small graduate. (White precipitate, presence of SILVER GROUP.) Filter, and wash the precipitate with a small quantity of cold water, adding the washings to the filtrate until its volume is about 40 ccm. (Precipitate, P. 12; filtrate, P. 21.)

Notes. — 1. Nonformation of a precipitate proves absence of silver and mercurous mercury, but not of lead (or thallous thallium), since $PbCl_2$ (and TlCl) are fairly soluble in water. Owing to the common-ion effect, the solubility of the chlorides is greatly decreased by the addition of HCl; but 20–40 mgm. Pb (and 5–15 mgm. Tl) may remain in solution, and thus escape detection in this group.

2. Since the subsequent precipitation of the copper and tin groups by H_2S must be made in a dilute HCl solution of known strength, a definite amount of HCl is added at this point and the solution is diluted to a known volume.

3. The addition of the first few drops of HCl may cause the precipitation of the white oxychlorides BiOCl and SbOCl; but these precipitates dissolve when the rest of the acid is added. If, however, the solution were largely diluted with water, the precipitate might again separate.

4. From an alkaline solution HCl might precipitate many other substances, as described in P. 3, N. 4. Such a solution is, therefore, first treated with HNO_3 (P. 3).

Procedure 12. — Pour repeatedly through the filter containing the HCl precipitate (P. 11) a portion of 10–20 ccm. boiling water. Wash the residue thoroughly with hot water. (Residue, P. 15; solution, P. 13.)

Procedure 13. — Add to the aqueous extract from the HCl precipitate (P. 12) one-fifth its volume of concentrated H_2SO_4; cool, shake the mixture, and allow it to stand for 5 minutes. (White precipitate, presence of LEAD.) Filter, wash the precipitate with H_2SO_4 (1.20) and then with a little water. (Precipitate, P. 14; filtrate, reject or test for thallium by * P. 13*a*.)

Note. — 1. $PbSO_4$ is slightly soluble in water, but, owing to the common-ion effect, much less so in dilute H_2SO_4; hence H_2SO_4 is added in excess to the solution and to the wash water.

* **Procedure 13a.** — To test for thallium add to the filtrate from the H_2SO_4 precipitate (P. 13) 2–3 ccm. KI solution. (Yellow precipitate, presence of THALLIUM.) If the solution becomes brown, owing to the liberation of free iodine, add a little H_2SO_3 solution.

**Notes.* — 1. Thallous iodide is much less soluble than the corresponding chloride, and its solubility is greatly decreased by KI, owing to the common-ion effect. PbI_2 is also difficultly soluble, but cannot be precipitated here, since lead has been removed by H_2SO_4 in P. 13. The presence of even 0.5 mgm. thallous thallium in 15 ccm. of solution may easily be detected in the cold by means of KI. Free iodine oxidizes thallous to thallic salts, but these, as well as the iodine itself, are reduced by H_2SO_3.

2. Thallous salts are oxidized to thallic salts rapidly by halogens and *aqua regia*, and slowly by hot concentrated HNO_3. Upon evaporating a thallic chloride ($TlCl_3$) solution and heating the residue at 120°, more or less complete reduction takes place by decomposition into TlCl and Cl_2. Pure thallic salts give no precipitate with HCl, thallous salts a white one; while mixtures of them give yellow precipitates ($TlCl_3.xTlCl$). For these reasons, even when the substance has been dissolved in HNO_3 and the solution has been evaporated as described in P. 4, thallium will be precipitated with this group by HCl if much of it is present.

Procedure 14. — Pour repeatedly through the filter containing the H_2SO_4 precipitate (P. 13) a 10–20 ccm. portion of a 10% ammonium acetate solution; add to the filtrate a few drops K_2CrO_4 solution and 2–5 ccm. dilute acetic acid. (Yellow precipitate, presence of LEAD.)

Notes. — 1. The solubility of $PbSO_4$ in solution of ammonium acetate ($NH_4C_2H_3O_2$) depends on the formation by metathesis of undissociated lead acetate, which is much less ionized than most other salts of the same type. On the addition of a chromate to this solution the much more difficultly soluble $PbCrO_4$ is precipitated, and is not dissolved by dilute acetic acid.

2. This confirmatory test is also applied to the $PbSO_4$ precipitate obtained in the analysis of the copper group (P. 26). In that case the precipitate may also contain bismuth, which would dissolve in ammonium acetate and give a yellow precipitate on the addition of K_2CrO_4; but this precipitate, unlike the $PbCrO_4$, dissolves readily in acetic acid.

Procedure 15. — Pour repeatedly through the filter containing the residue insoluble in hot water (P. 12) a 10–20 ccm. portion of NH_4OH

(0.96). (Black residue on the filter, presence of MERCUROUS MERCURY.) Acidify the filtrate with HNO_3. (White precipitate, presence of SILVER.)

Notes. — 1. The black residue produced by the action of NH_4OH on Hg_2Cl_2 is a mixture of finely divided mercury with the white mercuric compound $HgClNH_2$. The reaction is expressed by the equation:

$$Hg_2Cl_2 + 2NH_4OH = HgClNH_2 + Hg + NH_4Cl + 2H_2O.$$

The compound $HgClNH_2$ may be considered to be a derivative of $HgCl_2$, formed by replacing an equivalent of chlorine by the univalent radical NH_2.

2. It is to be noted that mercury will not be in the mercurous state, and therefore will not be precipitated with this group, if the substance has been heated with strong nitric acid or *aqua regia*.

3. AgCl dissolves readily in NH_4OH, owing to the formation of a soluble complex salt, $Ag(NH_3)_2Cl$, which in solution is largely dissociated into $Ag(NH_3)_2^+$ and Cl^- ions. This complex cathion has so slight a tendency to dissociate that in a normal solution of NH_4OH the ratio of its concentration to that of the simple Ag^+ ion is about 10^7.

4. HNO_3 reprecipitates the AgCl from its solution in NH_4OH, owing to the facts that the complex cathion is slightly dissociated according to the equation $Ag(NH_3)_2^+ = Ag^+ + 2NH_3$, and that the NH_3 combines with the added acid, forming NH_4NO_3, thus causing the complex cathion to dissociate further, until the Ag^+ concentration increases to such an extent as to make the product of it into the Cl^- concentration greater than the solubility product for AgCl.

5. The test is less delicate when the NH_4OH is neutralized with HCl, owing to the solubility of AgCl in strong chloride solutions, which arises, probably, from the formation of a salt with a complex anion, like $NH_4^+AgCl_2^-$.

Precipitation and Separation of the Copper and Tin Groups

Procedure 21. — Treat separately as follows the various acid solutions previously obtained (P. 11, 4, 2, 5, 6, 7, 8), each of which should contain 4 ccm. HCl (1.12) or 1.5 ccm. H_2SO_4 (1.84) and have a volume of about 40 ccm. Heat the solution in a conical flask nearly to boiling, and pass into it H_2S gas until it is saturated, and then for 10–15 minutes longer, keeping the solution at 70–90°. [*If the rarer elements are likely to be present, continue the precipitation in a pressure bottle as described in N. 3.] Cool the mixture; without filtering add to it 60 ccm. water, completely saturate it in the cold with H_2S gas, cork the

flask, shake it, and allow it to stand 15 minutes. Filter, and wash the precipitate with hot water. (Precipitate, P. 22; filtrate, P. 61.)

Notes. — 1. No sharp line can be drawn between the solubilities of the sulphides of the copper and tin groups and those of the iron group; they form rather a graded series in which the solubility of each member differs from that of the next only by a greater or less amount. Since now, owing to the effect of the added acid in reducing the ionization of the hydrogen sulphide, the solubility of any sulphide increases as the concentration of acid (or, more strictly, of hydrogen ion) in the solution increases, the line between precipitation and non-precipitation will fall at a point in the series dependent on the acid concentration and temperature. Thus, if arranged in the order in which they are precipitated from cold HCl solutions of decreasing concentration, the series is approximately as follows: arsenic, mercury and copper, antimony, bismuth and stannic tin, cadmium, lead and stannous tin, zinc, iron, nickel and cobalt, manganese. For reasons connected with the analysis of the separate groups, and for the reason that the separation is then a fairly sharp one, it has been found best to adjust the acid concentration so as to cause lead and stannous tin to precipitate and zinc to remain in solution.

2. The effect of acid on the precipitation of the various sulphides is explained by the Mass Action Law and Ionic Theory as follows: When a dilute solution, whether aqueous or acid, is saturated at a definite temperature with H_2S gas under the atmospheric (or any definite) pressure the H_2S as such always has the same concentration. This ionizes, however, to a slight extent into H^+ and HS^-, and to a still less extent into $2H^+$ and $S^=$. It is only the latter form of ionization that needs to be considered here. Now between the H_2S and its ions must be maintained the equilibrium expressed by the equation $(C_{H^+})^2 \times C_{S^=} = \text{const.} \times C_{H_2S}$; or, since in this case $C_{H_2S} = \text{const.}$, as just stated, it follows that also $(C_{H^+})^2 \times C_{S^=} = \text{const.}$ From this it is evident that when C_{H^+} is increased by the addition of acid to the solution, $C_{S^=}$ must be decreased in the proportion in which the square of C_{H^+} is increased; thus, if C_{H^+} is doubled, $C_{S^=}$ will be reduced to one-fourth. But in order that a sulphide — for example, of the formula $M^{++}S^=$ — may precipitate, the concentration product $C_{M^{++}} \times C_{S^=}$ must attain a value equal to the solubility product, which is the value of this concentration product which prevails in pure water in contact with the solid sulphide. The solubility product varies, however, with the nature of the sulphide and with the temperature; and therefore the acid concentration that will barely permit of precipitation when $C_{M^{++}}$ has

a definite value (for example, 1 mgm. in 100 ccm.) will be different for different sulphides and for the same sulphide at different temperatures. This acid concentration also varies with the nature of the acid, since the various acids are ionized to a different extent; thus zinc is precipitated from a fairly concentrated solution of acetic acid, since, owing to the slight ionization of this acid, the H^+ concentration is less than in a far more dilute solution of hydrochloric acid.

3. The solution is first saturated with H_2S at nearly the boiling temperature, because certain elements, especially arsenic in the higher state of oxidation (and the rarer elements, platinum and molybdenum), are only slowly and incompletely precipitated in the cold, and because the precipitates of almost all sulphides separate from hot solutions in a form better suited for filtration. In case precipitation seems to continue after the solution has become fully saturated with H_2S, it indicates that one of the elements just named may be present; and, to insure complete precipitation of the arsenic, the heating and passage of the gas must sometimes be continued for an hour longer. [*In case of molybdenum and the platinum elements, it is necessary, after most of the sulphide has separated, to cool the solution, to saturate it in the cold with H_2S in a stout bottle, to stopper the bottle with a cork securely held in place by wire, and to heat the bottle in a vessel of boiling water for an hour.] The solution is at first diluted to only about 40 ccm., because arsenic is more rapidly thrown out from rather strongly acid solutions, and because titanium would be precipitated as hydroxide if the solution were further diluted and were kept near the boiling temperature; moreover, bismuth and a moderate quantity of antimony do not precipitate as oxychloride at this dilution, but might do so if the solution were at once further diluted. The solution is finally diluted to 100 ccm., completely saturated in the cold, and allowed to stand, in order to cause the precipitation of even 1 mgm. of cadmium, lead, or stannous tin. Zinc, iron, nickel, and cobalt, on the other hand, do not precipitate at all under these conditions, even when 500 mgm. are present alone; and even 1 or 2 mgm. of any of them can be detected in the filtrate when large quantities of elements of the copper and tin groups are also present.

4. If at first a white or yellowish precipitate forms which immediately turns black with more H_2S, it indicates mercury. The white compound is $HgCl_2.2HgS$, and this is converted into HgS by the excess of H_2S. An orange precipitate separating from the hot, more concentrated solution shows antimony, or much cadmium (or selenium); a yellow one, arsenic or stannic tin. A yellow precipitate separating from the cold, more dilute solution shows cadmium. All the other sulphides are black

or brownish black. For the composition of the H_2S precipitates, see Table V. The quantity of sulphur combined with the metallic element, however, varies with the conditions of precipitation, owing to partial reduction, in the cases of arsen*ic* arsenic and antimonic antimony [*and of gold, selenium, tellurium, and probably molybdenum]. The extent to which the sulphides are combined with water and with hydrogen sulphide is also variable and in general unknown.

5. A white, finely divided precipitate of free sulphur will be formed if the solution contains substances capable of oxidizing H_2S. The most important of these likely to be present are ferric salts, chromates, [*vanadates], permanganates, and chlorates. Nitric acid, if moderately concentrated, would also destroy the H_2S; and for this reason it must have been removed as directed in P. 4. The reduction by H_2S of ferric salts to ferrous is attended by a change in color from yellow to colorless; of chromates to chromic salts, from orange to green; [*of vanadates to vanadyl salts, from yellow to blue]; and of permanganates to manganous salts, from purple to colorless.

Procedure 22. — Transfer the H_2S precipitate (P. 21) to a small casserole, add to it 10–25 ccm. ammonium monosulphide (if the original substance was treated with HNO_3 in P. 3), or 5–10 ccm. ammonium polysulphide (if it was dissolved in water alone), cover the dish, and warm the mixture slightly (to 40–60°) for about 10 minutes with frequent stirring. Add 10 ccm. water, filter, and wash once with hot water. [If the residue is considerable in amount and much has been extracted from it by this treatment, as indicated by its appearance, or as determined in P. 41, warm it again with ammonium monosulphide or polysulphide, and filter, collecting the filtrate separate from the first one.] Wash the residue thoroughly with hot water, to which, in case the precipitate tends to pass through the filter, about 5% solid NH_4NO_3 should be added. (Residue, P. 23; solutions, P. 41.)

Notes. — 1. In separating the copper and tin groups it is better to use (colorless) ammonium monosulphide rather than (yellow) polysulphide whenever the H_2S precipitate must contain any tin and most of any antimony present in the state of the higher sulphide (SnS_2 or Sb_2S_5). This is the case when hot concentrated nitric acid was used originally in dissolving the substance, but may not be so when water alone (or HCl) was used; hence the directions as to the choice between the two solvents. The polysulphide has the disadvantage that it dissolves a not inconsiderable quantity of CuS and HgS, thus making the tests for copper and mercury less delicate, and making it more difficult

to determine from the color of the HCl precipitate obtained from the ammonium sulphide solution in P. 41 whether or not elements of the tin group are present. The polysulphide must, nevertheless, be used if tin may be present as SnS, or much antimony as Sb_2S_3; for in the monosulphide SnS is almost insoluble and Sb_2S_3 is only moderately soluble (50–100 mgm. Sb in 10 ccm. of the reagent).

2. In order that the separation of the copper and tin groups by ammonium sulphide may be as complete as possible, it is necessary to employ a concentrated reagent highly charged with hydrogen sulphide, and containing, in the case of the polysulphide, an appropriate excess of sulphur. Suitable reagents are prepared by completely saturating a measured volume of NH_4OH of specific gravity 0.90 with H_2S in the cold, adding a fresh portion of NH_4OH (0.90) equal to two-thirds of the original volume, and diluting the mixture with an equal volume of water. From this solution, which constitutes "ammonium monosulphide," the "ammonium polysulphide" is prepared by dissolving in 1 liter of it 25 grams of flowers of sulphur. These reagents, especially the monosulphide, should be kept as far as possible out of contact with the air, which is conveniently done by storing them in small, completely filled, glass-stoppered bottles; for the oxygen of the air destroys the sulphide with liberation of sulphur, which at first combines with the still unchanged sulphide, but precipitates later when the oxidation becomes more complete. The monosulphide reagent is a solution of $(NH_4)_2S$ and of the products of its hydrolysis, NH_4SH, NH_4OH, and a little H_2S. The polysulphide contains in addition various polysulphides of the forms $(NH_4)_2S_{2-5}$ and $(NH_4)HS_{2-5}$ in unknown proportions.

3. The action of ammonium sulphide in dissolving the sulphides of the tin group depends on the formation of soluble salts of sulphoacids with complex anions. When the monosulphide is used, the reactions are as follows:

$$\left\{\begin{matrix}As_2S_3\\Sb_2S_3\end{matrix}\right\} + 3(NH_4)_2S = 2\left\{\begin{matrix}(NH_4^+)_3AsS_3^{\equiv}\\(NH_4^+)_3SbS_3^{\equiv}\end{matrix}\right\}$$

$$\left\{\begin{matrix}As_2S_5\\Sb_2S_5\end{matrix}\right\} + 3(NH_4)_2S = 2\left\{\begin{matrix}(NH_4^+)_3AsS_4^{\equiv}\\(NH_4^+)_3SbS_4^{\equiv}\end{matrix}\right\}$$

$$SnS_2 + (NH_4)_2S = (NH_4^+)_2SnS_3^{=}.$$

The excess of sulphur in the polysulphide oxidizes the lower sulphides (As_2S_3, Sb_2S_3, SnS) to the same sulphosalts as are obtained by dissolving the higher sulphides (As_2S_5, Sb_2S_5, SnS_2) in ammonium monosulphide. It will be seen that these sulphosalts are analogous to the salts of the familiar oxygen acids of these elements, the difference being that sulphur has replaced oxygen. *Analogous sulphosalts are formed with plati-

num, gold, and molybdenum, such as $(NH_4)_2PtS_3$, $(NH_4)_3AuS_3$, and $(NH_4)_2MoS_4$. Tellurium and selenium probably form similar compounds; but they may also combine directly with the ammonium sulphide in the same way as sulphur does, forming such compounds as $(NH_4)_2SSe_x$.

4. When ammonium monosulphide is used, 500 mgm. of any of the common tin-group elements, in the form of higher sulphide, dissolve in 25 ccm. of the reagent, provided this has been prepared as described in N. 2. When the polysulphide is used, 500 mgm. of any of the common tin-group elements, whether present as the higher or lower sulphide, dissolve in 10 ccm. of the reagent. The quantity of SnS and Sb_2S_3 dissolved by the polysulphide increases with its concentration and the excess of sulphur which it contains. A reagent containing a greater excess of sulphur is not used, however, since this would dissolve more CuS and HgS.

*5. Of the rarer elements, gold and platinum divide themselves in the ammonium sulphide treatment between the solution and the residue in a proportion which depends in large measure on the other elements which are present with them. They may, therefore, be found mainly either with the copper or with the tin group, and should be tested for in the course of the analysis of each group. Molybdenum dissolves in moderate quantity in either ammonium monosulphide or polysulphide, but when a quantity as large as 50 mgm. is present much of it remains with the copper group; yet there is no danger of not finding a considerable part of it in the tin-group solution, and its presence in the copper-group residue does not interfere with the detection of any of the elements, since it is not precipitated by any of the reagents used. When molybdenum is present, even in as small a quantity as 1 mgm., the ammonium sulphide solution has an orange-red color; and this becomes very deep when a moderate quantity is present. Selenium and tellurium pass completely, or almost completely, into the ammonium sulphide solution.

6. Even when a quantity of only 1 or 2 mgm. of arsenic or antimony is present with a large quantity (even 500 mgm.) of an element of the copper group, enough is extracted by either the monosulphide or polysulphide to be detected in the subsequent tests. With tin, however, the separation is imperfect; for, when a large quantity of elements of the copper group and only 3–5 mgm. of tin are present, the whole of this may remain undissolved; indeed, when much cadmium is present and the tin is in the stannous state, as much as 15 mgm. of the latter may be wholly left in the residue, even when the polysulphide is used. On this account it is necessary to test for tin in the course of the analysis of the copper group.

7. Of the sulphides of the copper group none dissolve to a significant extent in the monosulphide. Considerable CuS (5–10 mgm.) and a little HgS (0.5–1.0 mgm.) may, however, dissolve in the polysulphide when the substance contains a large quantity of these elements. Yet when 2 mgm. of either of these elements are present it can be detected in the analysis of the copper group, even when the polysulphide is used, provided only one treatment with it has been made.

8. Some sulphides, especially CdS, upon washing pass through the filter in the colloidal condition; the addition of a salt, such as NH_4NO_3, prevents this by coagulating the colloidal particles.

Analysis of the Copper Group

Procedure 23. — To the residue from the ammonium sulphide treatment (P. 22) in a casserole add 10–20 ccm. of a mixture of one volume HNO_3 (1.20) and two volumes water, heat to boiling, and boil gently for a minute or two. (Black residue, possible presence of MERCURY.) Filter and wash. (Residue, P. 24; solution, P. 26.)

Notes. — 1. Boiling HNO_3 of this concentration dissolves the sulphides of lead, bismuth, copper, and cadmium almost immediately, and is therefore preferable to a more dilute acid, with which the reaction would require for its completion several minutes' boiling. Scarcely any HgS is dissolved by the above treatment, unless the boiling is long continued.

2. Moderately concentrated HNO_3 dissolves sulphides much more rapidly than HCl or H_2SO_4 of the same concentration; for with the latter acids the sulphide ion is removed from the solution only by combination with the hydrogen ion forming slightly ionized H_2S and by the volatilization of the latter, while with HNO_3 the sulphide ion (or the H_2S in equilibrium with it) may also be destroyed by oxidation to ordinary sulphur. The oxidizing effect of HNO_3 is, however, considerable only when it is hot and moderately concentrated.

3. That HgS, unlike the other sulphides, does not dissolve in the dilute HNO_3 is doubtless due to the much smaller concentration of its ions in its saturated solution and to the fact that at this small concentration the sulphide ion (or the H_2S in equilibrium with it at a correspondingly small concentration) is oxidized only very slowly by the dilute HNO_3. HgS is, however, readily dissolved by more vigorous oxidizing agents, such as *aqua regia* or bromine water, since they react rapidly with sulphide ion (or with H_2S) even when its concentration is very small.

4. If more concentrated HNO_3 be used, or if the acid become concentrated by long boiling, the black HgS is dissolved in part, and the remainder is converted into a heavy, white, difficultly soluble compound ($Hg(NO_3)_2.2\,HgS$).

5. When much lead, copper, or bismuth is present the sulphur formed will generally enclose enough of the undissolved sulphide to give it a black color. [* Moreover, PtS_2 and Au or Au_2S if present are not dissolved by the HNO_3.] A black residue is therefore not necessarily HgS and must be further tested for mercury as described in P. 24.

6. Some sulphur is always oxidized to H_2SO_4 by the boiling HNO_3, but, even in the presence of much lead, $PbSO_4$ is not precipitated, owing to its moderate solubility in HNO_3.

7. Any SnS or SnS_2 not extracted by the ammonium sulphide treatment will be converted by HNO_3 into metastannic acid, most of which remains undissolved. Therefore, even a light-colored residue must be carefully collected if tin is to be tested for in this group.

Procedure 24. — Transfer the residue undissolved by HNO_3 (P. 23), with the filter if necessary, to a casserole, add 10–40 ccm. saturated Br_2 solution, cover the dish, and warm slightly for 5–10 minutes, with frequent stirring. Boil the mixture until the bromine is expelled, and filter. (Residue, P. 25.) [*If the solution is yellow, indicating that gold or platinum may be present, treat it by *P. 24*a*, and then proceed as follows.] Cool the solution, and add to it a few drops of HCl (1.12) and a 2% $SnCl_2$ solution, at first drop by drop; then add several cubic centimeters of a 10% $SnCl_2$ solution. (White precipitate turning gray, or gray precipitate, presence of MERCURY.) (Residue and solution, reject.)

Notes. — 1. Bromine water dissolves the sulphides of mercury, platinum, and gold, but leaves in the residue any metastannic acid. In case tin need not be tested for at this point, the residue may be more quickly dissolved by warming it with HCl (1.12) and adding gradually a little solid $KClO_3$; since metastannic acid is soluble in HCl, this then passes into solution with the mercuric salt.

2. In the final test for mercury HCl is added to prevent the precipitation of a basic tin salt when the $SnCl_2$ reagent is diluted, and to cause the formation at first of white Hg_2Br_2 or Hg_2Cl_2. For the latter reason, also, dilute $SnCl_2$ solution is added drop by drop to the cold solution. By the excess of $SnCl_2$ the white precipitate is reduced to gray, finely divided mercury.

3. The presence of mercury at this point does not show that it was originally in the mercuric state, except in case the substance was dissolved without the use of hot or concentrated HNO_3. If it is desired to determine in which state the mercury was originally present, a solution of the substance in water, in dilute H_2SO_4, or in cold, very dilute HNO_3 must be prepared and analyzed for mercurous and mercuric mercury by the regular process, beginning with P. 11.

*4. Platinum and gold compounds, if not removed, are reduced by $SnCl_2$, the former giving a reddish brown solution and the latter a dark-colored or purple precipitate of metallic gold. The presence of these elements would thus interfere with, or prevent the detection of, mercury, and it is therefore directed to remove them.

***Procedure 24a.** — To the solution of the sulphides in bromine water (P. 24) add about 0.5 gram solid KCl and 1–2 ccm. HCl (1.12), evaporate until KCl crystallizes out, cool, and add water drop by drop until almost all the KCl has dissolved. (Yellow precipitate, presence of PLATINUM.) Filter and wash with a little saturated KCl solution. Confirm the presence of platinum in the precipitate by *P. 43*a*. To the filtrate add 10% NaOH solution till alkaline, and then about 1 ccm. more. Then add saturated oxalic acid ($H_2C_2O_4$) solution until the solution becomes distinctly acid, dilute to about 15 ccm., and digest on a steam bath for 10–15 minutes. (Purplish black or dark yellow precipitate, presence of GOLD.) Filter. Reject the precipitate. Test the filtrate for mercury with $SnCl_2$ solution by the last part of P. 24.

Note. — 1. For notes upon this process, see under *P. 43*a* and 43*b*. By means of it can be detected 1 mgm. of gold or platinum in the presence of much mercury (at least 200 mgm.), or 1 mgm. of mercury in the presence of much gold or platinum.

Procedure 25. — If it is necessary to extract tin (see N. 1 below) from the residue undissolved by HNO_3 and bromine water (P. 24), digest it, if it is still dark-colored, with another portion of bromine water to extract the rest of the mercury, filter, reject the filtrate, and warm the residue slightly with 2–5 ccm. ammonium monosulphide, filter, and unite the solution with the main ammonium sulphide solution obtained in P. 22.

Note. — 1. If it is desired to detect with certainty the presence in the substance of a quantity of tin smaller than 5 mgm., and if elements of the copper group are present in large quantity (100–500 mgm.), it

is necessary to recover the tin that remained with the copper group; for, as stated in P. 22, N. 5, a quantity of tin as large as 5 mgm. (or even larger when stannous tin and cadmium are both present) may remain entirely in the residue undissolved by ammonium sulphide when this residue is large. By extracting the tin as described in this procedure and uniting it with the main solution of the tin group 2 mgm. of tin can be detected.

Procedure 26. — To the HNO_3 solution (P. 23) add 2–3 ccm. concentrated H_2SO_4, and evaporate in a casserole until fumes of H_2SO_4 begin to come off. Cool and pour into 10–15 ccm. cold water, rinsing out the casserole with the same solution. Cool again, shake, and allow the mixture to stand 5 minutes, but not much longer. (Finely divided white precipitate, presence of LEAD; but a coarsely crystalline precipitate may be due to bismuth.) Filter and wash the precipitate with H_2SO_4 (1.20), and finally with a little water. (Precipitate, P. 14, to confirm the presence of lead; filtrate, P. 27.)

Notes. — 1. $PbSO_4$ is somewhat soluble both in water and in concentrated H_2SO_4, but much less so in moderately dilute H_2SO_4, its solubility being scarcely appreciable in mixtures containing one volume of H_2SO_4 (1.84) and two to six volumes of water. That the solubility in dilute H_2SO_4 is less than that in water is due mainly to the common-ion effect. Concentrated H_2SO_4 is, of course, an entirely different solvent. $PbSO_4$ dissolves fairly readily in dilute HNO_3 (or in dilute HCl), owing to metathesis arising mainly from the tendency to form un-ionized H_2SO_4; hence, although this effect of HNO_3 is partly counteracted by the presence of much H_2SO_4, yet, to ensure complete precipitation of $PbSO_4$, the HNO_3 must be removed by evaporation.

2. When much bismuth is present it ordinarily is dissolved at first when the water is added to the concentrated H_2SO_4, provided the mixture is kept cold; but from this solution a coarsely crystalline precipitate of an oxysulphate, such as $(BiO)_2SO_4$, separates slowly upon standing in the cold but almost immediately upon heating, and to such an extent that there may remain in solution not more than 50 mgm. of bismuth. If such a precipitate has separated with the $PbSO_4$, filter, treat the filtrate by P. 27, and dissolve the precipitate by pouring repeatedly through the filter a 5–10 ccm. portion of HCl (1.12), and test the solution so obtained for lead by following P. 26 and P. 14.

Procedure 27. — To the H_2SO_4 solution (P. 26) add NH_4OH slowly until a strong odor of it persists after shaking. (White precipi-

tate, possible presence of BISMUTH; blue solution, presence of COPPER.) Shake to cause coagulation, filter, and wash the precipitate. (Precipitate, P. 28; filtrate, P. 29 and 30.)

Notes. — 1. The precipitate produced by NH_4OH may also consist of $Fe(OH)_3$, or of other hydroxides of the iron group, if these elements were carried down in the H_2S precipitate or were not completely removed from it by washing. The formation of a small precipitate is, therefore, not a sufficient proof of the presence of bismuth, and the confirmatory tests must be applied. Antimony which, like bismuth, gives with water a precipitate of an oxychloride cannot be present in sufficient quantity to be precipitated by NH_4OH.

2. That $Cd(OH)_2$ or $Cu(OH)_2$, though only very slightly soluble in water, dissolves in NH_4OH is due to the conversion of the Cd^{++} or Cu^{++} ion in the saturated solutions into the complex cathion $Cd(NH_3)_4^{++}$ or $Cu(NH_3)_4^{++}$, which is formed by combination of the simple ion with un-ionized ammonia. These complex cathions have an extremely small ionization tendency; thus for cadmium in a normal NH_4OH solution the ratio of the concentration of the complex to the simple ion is about 10^7. The solubility of these hydroxides in NH_4OH is greatly increased by the presence of ammonium salts, since these salts, owing to the common-ion effect, greatly reduce the ionization of the NH_4OH, and therefore the OH^- concentration in the solution, thus enabling the Cd^{++} or Cu^{++} concentration, and therefore also the corresponding complex ion concentration, to attain a much larger value than in the saturated solutions of $Cd(OH)_2$ or $Cu(OH)_2$ in NH_4OH alone. It will be noticed that four distinct equilibria are involved — that between solid $Cd(OH)_2$ or $Cu(OH)_2$ and its ions; that between Cd^{++} or Cu^{++}, NH_3, and $Cd(NH_3)_2^{++}$ or $Cu(NH_3)_4^{++}$; that between NH_4OH, NH_3, and H_2O; and that between NH_4OH, NH_4^+, and OH^-. It may be further mentioned that, since in any dilute solution the concentration of the water is substantially constant, the concentration of any hydrate (like NH_4OH) is proportional to that of the anhydrous substance (NH_3).

Procedure 28. — Dissolve the NH_4OH precipitate (P. 27) by pouring a little HCl (1.12) through the filter, evaporate off the acid almost completely, leaving the residue only barely moist with it, add 1–2 ccm. water, pour the solution into a flask containing 100 ccm. water heated to 50–70°, and allow the mixture to stand 2 or 3 minutes. (White precipitate, presence of BISMUTH.) Filter, wash once, and pour through the filter a freshly prepared solution of sodium stannite. (Black residue, presence of BISMUTH.)

Notes. — 1. The white precipitate formed in the first confirmatory test for bismuth is BiOCl, which is produced by the hydrolysis of $BiCl_3$. If HCl, the other product of the hydrolysis, is present in the solution, the reaction will not be complete, and a greater or less quantity of bismuth will remain in solution and thus escape detection. This quantity increases rapidly with the acid concentration in accordance with the Law of Mass-Action. For this reason, if the presence of half a milligram of bismuth in the precipitate is to be detected, the HCl must be removed by evaporation so completely that not more than 0.2 ccm. remain, and the solution must be added to a large volume of water. Warm water is used, because the precipitation of BiOCl takes place more rapidly at the higher temperature.

2. The solution of sodium stannite (Na_2SnO_2) is prepared when needed by adding a 10% NaOH solution to a 10% $SnCl_2$ solution until the $Sn(OH)_2$ first formed is dissolved. The solution must be freshly prepared, because it decomposes spontaneously into sodium stannate (Na_2SnO_3) and metallic tin, and because it oxidizes in contact with air to sodium stannate. SnO_2H_2 is an example of a so-called amphoteric substance — one which acts either as a base or an acid, as is shown by its solubility in both acids and alkalies.

3. The final test with sodium stannite depends on the reduction of BiOCl to black metallic bismuth. The test is an extremely delicate one, and by it may be detected a quantity of bismuth so small as to produce only a scarcely visible turbidity of BiOCl; for, when the precipitate in such a solution is collected on a filter and treated with stannite, the black color of the bismuth is very apparent. Antimony oxychloride, even if present, is not blackened by the stannite. The NH_4OH precipitate itself might be directly tested with this reagent; for the other reducible substances, like $Fe(OH)_3$, $Pb(OH)_2$, or $Cu(OH)_2$, that might possibly be present in that precipitate are not reduced by short contact with stannite solution in the cold. It is, however, often desirable to get the double indication of the presence of bismuth, as furnished by the precipitation of the oxychloride by water and by its blackening with the sodium stannite.

Procedure 29. — Acidify one-fourth of the NH_4OH solution (P. 27) with acetic acid, add 2–3 drops 3% $K_4Fe(CN)_6$ solution, and allow the mixture to stand for several minutes. (Red precipitate, presence of COPPER.) If it is uncertain whether there is a precipitate, pour the solution through a filter and wash with a little water. (Pink color on the filter, presence of COPPER.)

Notes. — 1. The confirmatory test for copper depends on the precipitation of red cupric ferrocyanide, $Cu_2Fe(CN)_6$. Since this test is a more delicate one than the formation of a blue color with NH_4OH (P. 27), it should be tried even when the NH_4OH solution is colorless. Cadmium is also precipitated by $K_4Fe(CN)_6$; but the precipitate is white, and does not prevent the pink color of the copper compound from being detected, provided only a small quantity of $K_4Fe(CN)_6$ is added; for the copper salt, owing to its smaller solubility, is first precipitated.

2. Nickel, like copper, gives a blue solution with excess of NH_4OH; but even if present it would give a greenish white, not a red precipitate, with $K_4Fe(CN)_6$. Aside from copper, only the rarer elements uranium and molybdenum give red precipitates with this reagent; but they do not do so in an acetic acid solution, such as is obtained in the procedure.

Procedure 30. — To the remainder of the NH_4OH solution (P. 27 and 29) add solid KCN till the blue color disappears, and pass in H_2S gas for about half a minute. (Flocculent yellow precipitate, presence of CADMIUM.) (Precipitate and solution, reject.)

Notes. — 1. By the addition of KCN the copper salt is reduced from the cupric to the cuprous state and then combines with the excess of KCN to form the complex salt $K^+Cu(CN)_2^-$ (potassium cuprocyanide). This result is due to the fact that cupric cyanide tends to decompose spontaneously into cuprous cyanide and cyanogen, and that this reaction takes place completely in KCN solution, owing to removal of the cuprous cyanide by combination with the excess of KCN. In the presence of NH_4OH the cyanogen is not evolved as a gas, but reacts with it, forming cyanate (NH_4CNO) and cyanide and other more complex products. The fact that neither CuS nor Cu_2S is precipitated from this solution by an alkaline sulphide shows that neither the Cu^{++} nor Cu^+ concentration is sufficient to cause the value of the solubility product to be attained. The extremely small Cu^+ concentration is due to the very slight ionization tendency of the complex anion $Cu(CN)_2^-$: thus it has been estimated that in a normal KCN solution the ratio of the concentration of the complex anion to that of the simple Cu^+ ion is about 10^{26}.

2. The cadmium ammonia salt is also converted by KCN into a complex cyanide, namely, $K^+_2Cd(CN)_4^=$ (potassium cadmicyanide), since its complex anion has a much smaller ionization tendency than the cathion $Cd(NH_3)_4^{++}$; thus in a normal KCN solution the ratio of the concentration of the complex anion to that of the simple Cd^{++} ion is

about 10^{17}. Yet this complex anion is sufficiently dissociated into Cd^{++} ion to cause the solution to become saturated with CdS when an alkaline sulphide is added.

3. A very small black precipitate (which may be due to HgS or PbS) may sometimes be produced in the final test for cadmium with H_2S; but, provided the analysis has been properly conducted, not in sufficient quantity to prevent the yellow color of 1 or 2 mgm. of CdS from being seen. In case a black precipitate is produced, and thus prevents a positive conclusion as to the entire absence of cadmium, the precipitate may be treated, in order to eliminate the black sulphide, as follows: Boil the precipitate for about 5 minutes with about 15 ccm. of a mixture of one volume of H_2SO_4 (1.20) with four volumes of water, filter, cool the filtrate, add to it three times its volume of water, and pass H_2S into it for 5–10 minutes. A yellow precipitate of CdS should then be obtained, if cadmium is present.

Analysis of the Tin Group

Procedure 41. — Dilute in a small flask the first portion of the ammonium sulphide solution (P. 22) with about 20 ccm. water, make it distinctly acid with HCl, and warm it slightly for 5 minutes with frequent shaking to coagulate the precipitate. (Fine, not flocculent, white or pale yellow precipitate, absence of TIN GROUP; deep yellow or orange flocculent precipitate, presence of TIN GROUP.) Treat the second portion of the ammonium sulphide solution (P. 22) in the same way, and unite the precipitate, if considerable in amount, with the first one. Filter out and wash the precipitate, using suction, finally sucking it as dry as possible. (Precipitate, P. 42; filtrates, reject.)

Notes. — 1. Much time is saved by determining at this point whether or not any element of the tin group is present. When ammonium monosulphide has been used, there is usually no difficulty in drawing a definite conclusion in regard to this from the size and appearance of the HCl precipitate; for in the absence of the tin group only a very small, nearly white precipitate of finely divided sulphur separates. When, however, ammonium polysulphide has been used, it may not be possible to decide as to the presence or absence of a small quantity (1–5 mgm.) of arsenic, antimony, or tin; for not only is a fairly large precipitate of sulphur then obtained, but it may be darkened in color by the presence of CuS or HgS: yet when the precipitate is nearly white, and finely divided or granular, the conclusion can be drawn at once that no element of the tin group is present in quantity as large as 1 mgm.; and when it has

a pronounced yellow color (indicating arsenic or tin) or an orange-red color (indicating antimony) the conclusion can be drawn that one of these elements is present. In this connection it may be mentioned that a mixture of SnS_2 and Sb_2S_5 does not always have a color intermediate between those just mentioned, but may be brown or dark gray.

2. When, however, the HCl precipitate from a polysulphide solution is fairly small and is dark brown (indicating copper) or dark gray or black (indicating mercury or one of the rarer elements) or of unpronounced yellow or orange color, so as to make any conclusion as to the tin group doubtful, the precipitate is best treated as follows: Heat it with 15–20 ccm. NH_4OH (0.96) almost to boiling for 5 minutes and filter; test the precipitate for copper by P. 23, 28, and 30 if it has not already been found present; add to the filtrate a few drops of ammonium monosulphide, filter out any precipitate, heat the filtrate to boiling, make it acid with HCl, shake, filter out the precipitate, and treat it by P. 42 as usual. The character of the HCl precipitate thus obtained will clearly indicate the presence or absence of the tin group; for by the treatment with NH_4OH the excess of sulphur originally present and any CuS is left undissolved, and by the $(NH_4)_2S$ added to the solution any mercury present is precipitated, so that the HCl precipitate can contain only sulphides of the tin group and a very little sulphur. As_2S_5, Sb_2S_5, and SnS_2 all dissolve in NH_4OH (though in the cases of Sb_2S_5 and SnS_2 less abundantly than in ammonium sulphide), owing to the formation of a mixture of salts of the intermediate sulphoacids, such as H_3AsO_3S and $H_3AsO_2S_2$. The addition of $(NH_4)_2S$ to the NH_4OH solution and the heating serve to convert these into more highly sulphurated acids, from which HCl will then precipitate the simple sulphides completely. — The incidental removal of the small amounts of CuS and HgS by the NH_4OH treatment is not necessary as far as the analysis of the tin group is concerned, since their presence does not interfere with the detection of even 1 mgm. of arsenic, antimony, or tin; but it does enable 1 or 2 mgm. of copper to be detected which might otherwise be lost.

3. When the HCl is added to the solution of the sulphosalts, the corresponding sulphoacids which are liberated decompose immediately into H_2S and the solid sulphides, which are now necessarily in the higher state of oxidation, since the lower sulphides, if originally present, have been oxidized by the polysulphide. The fact that the sulphoacids decompose while the sulphosalts are stable is a consequence of the Mass-Action Law, which, when applied to the dissociation of the complex anions taking place according to the equations,

$$SnS_3^{=} = SnS_2 + S^{=},\quad 2AsS_4^{\equiv} = As_2S_5 + 3S^{=},\quad 2SbS_4^{\equiv} = Sb_2S_5 + 3S^{=},$$

evidently requires that these decompose to a greater extent into the un-ionized sulphides (SnS_2, etc.) the smaller the concentration of the $S^=$ ion in the solution. Now in the solution of the largely ionized $(NH_4^+)_2S^=$ there is a fairly large concentration of $S^=$ ion; but when the solution is made acid with HCl, the $S^=$ ion is, for the most part, converted by the relatively large concentration of the H^+ ion into the slightly ionized substances HS^- and H_2S; and consequently the concentration of the un-ionized sulphides in the solution becomes great enough to exceed the solubility value, and the solid sulphides separate out.

Procedure 42. — Transfer the precipitated sulphides dried by suction (P. 41) to a wide test tube, add from a small graduate exactly 10 ccm. HCl (1.20), and heat nearly but not quite to boiling (preferably by immersing the test tube in hot water or on a steam bath) for about 10 minutes with frequent stirring. Add 5 ccm. water from a graduate containing 40 ccm. water, filter, wash once with about 5 ccm. water from the graduate, collecting this wash water with the filtrate; remove the filtrate, and add to it the water remaining in the graduate; wash the residue with HCl (1.12). (Residue, P. 43; filtrate, P. 45.)

Notes. — 1. If a much weaker HCl solution than the acid of specific gravity 1.20 is used, or if the acid becomes diluted by an unnecessary quantity of water left in the precipitate, much Sb_2S_5 will be left undissolved. Even with the strong acid some Sb_2S_5 may remain undissolved, especially when a large quantity is present, in which case the residue if small in amount will have an orange color. This small quantity of Sb_2S_5 would be only very slowly removed by further treatments with HCl; it does not, however, interfere with the subsequent tests for arsenic. Moreover, when only a small quantity of Sb_2S_5 is originally present, a large proportion of it is extracted, so that it will not escape detection. Sb_2S_5 dissolves with formation of $SbCl_3$ and liberation of sulphur: SnS_2 with formation of $SnCl_4$.

2. If the solution be kept just below the boiling point during the treatment with HCl, the amount of As_2S_5 which dissolves in 10 minutes is insignificant; but this is no longer true if the solution be allowed to boil, for the boiling rapidly expels from the solution the H_2S liberated from the other sulphides or by slight decomposition of the As_2S_5 itself, and thus enables the decomposition of the latter to proceed further.

3. As_2S_3 is more rapidly dissolved by HCl than is As_2S_5. If the former can be present in the precipitate, which can occur only when HNO_3 or *aqua regia* was not used in dissolving the original substance

and if ammonium monosulphide was employed for separating the copper and tin groups, the procedure should be modified as follows: After the addition of HCl to the sulphides saturate with H_2S in the cold, and then heat nearly but not quite to boiling for 10 minutes, passing a slow current of H_2S gas through the mixture. Under these conditions scarcely any As_2S_3 dissolves.

4. About 5 ccm. water are added to the HCl solution to enable it to be filtered. If more be added, and the H_2S has not been completely expelled from the solution, a precipitate of Sb_2S_3 may separate. If this happens after the filtration, it does, of course, no harm.

5. Care must be taken to follow closely the directions in regard to the quantities of HCl and water used; for the subsequent separation of antimony and tin (P. 45) depends upon a proper concentration of the acid.

6. The greater part of any CuS and HgS present will be dissolved by the HCl, and will be precipitated later with the Sb_2S_3 (P. 45). A little remains with the As_2S_5, but this does not interfere with the tests for arsenic. *Of the precipitates of the rarer elements, PtS_2, $Au_2S_{3\text{-}6}$, Se, and MoS_3 are dissolved by the HCl scarcely at all, and TeS_2 only to a small extent. The dissolving of the last, like that of As_2S_3, can be entirely prevented by passing a slow current of H_2S through the hot HCl solution.

Procedure 43. — Warm the residue from the HCl treatment (P. 42) with 5–10 ccm. HCl (1.12), adding solid $KClO_3$ in small portions until the reaction is complete; filter off the sulphur, and evaporate the solution to about 2 ccm. [If the solution is still distinctly yellow, or if a yellow precipitate has separated, test for and remove platinum by *P. 43*a*, and treat the filtrate as follows.] Add NH_4OH gradually until the solution after shaking smells of it; cool, filter off and reject any precipitate. Add to the filtrate about one-third its volume of NH_4OH (0.90) and several drops of magnesium ammonium chloride reagent, and shake. If no precipitate appears, rub the walls of the test tube gently with a glass rod for a minute or two. (White crystalline precipitate, presence of ARSENIC.) Collect the precipitate on a filter and wash it once with NH_4OH (0.96). (Precipitate, P. 44; filtrate reject, or test for gold, selenium, tellurium, and molybdenum, by *P. 43*b*).

Notes. — 1. The main reaction between $KClO_3$ and concentrated HCl is the formation of Cl_2; the yellow color results from the formation of a small proportion of chlorine dioxide, ClO_2.

2. As_2S_5, though only very slowly dissolved by HCl alone, is dissolved rapidly by it in the presence of Cl_2, because of the destruction of the H_2S, one of the reaction products, by oxidation. It is dissolved with formation of H_3AsO_4; $AsCl_5$ has never been shown to exist. When, as here, arsenic is present in the higher state of oxidation, solutions of it may be boiled without loss of an amount of arsenic significant in qualitative analysis.

3. A white precipitate, obtained on adding NH_4OH, may arise from the presence of mercury. The NH_4OH solution may contain not only arsenic, but also certain rare metals and the small quantities of copper (if ammonium polysulphide was used), antimony, and stannic tin that were not dissolved out of the sulphide precipitate by HCl.

4. The test for arsenic depends on the formation of magnesium ammonium arsenate, $Mg^{++}(NH_4)^+AsO_4^{\equiv}$. This salt is somewhat soluble in water, and therefore the solution tested should be fairly concentrated. Owing to hydrolysis (into NH_4OH and $Mg^{++}HAsO_4^{=}$), the precipitate is much more soluble in water than in a strong NH_4OH solution; hence the addition of a large quantity of the latter. Like other crystalline precipitates, it tends to form a supersaturated solution. Precipitation is promoted by agitation, by rubbing the walls of the tube with a glass rod, and by increasing the degree of supersaturation, which is done by concentrating and adding NH_4OH. Provided these precautions are taken and the total volume of the final solution does not exceed 5 ccm., the presence of even half a milligram of arsenic can be detected. Care must be taken not to scratch the glass by violent rubbing, since the powdered glass may be mistaken for the $MgNH_4AsO_4$ precipitate.

5. The magnesium ammonium chloride reagent contains $MgCl_2$ and NH_4Cl. The presence of the latter salt prevents the precipitation of $Mg(OH)_2$ by NH_4OH, by reducing the OH^- concentration.

***Procedure 43a.** — Evaporate the solution of the sulphides in HCl and $KClO_3$ (P. 43) until KCl crystallizes out, cool, and add water drop by drop until the KCl just redissolves. (Yellow precipitate, presence of PLATINUM.) Filter, wash the precipitate with a little cold saturated KCl solution, and treat the filtrate by P. 43 to detect and remove arsenic. Dissolve the precipitate by pouring repeatedly a 5–10 ccm. portion of hot water through the filter, and add to the solution a few drops of KI solution. (Deep red color, presence of PLATINUM.)

Notes. — 1. Potassium chlorplatinate, $K^+_2PtCl_6^{=}$, is fairly soluble in water, but much less so in a saturated KCl solution, owing to the common-ion effect.

2. The deep red color formed on the addition of KI to K_2PtCl_6 is due to the formation of K_2PtI_6 in solution. When the K_2PtCl_6 is present in excess a black precipitate of PtI_4 separates, but this dissolves readily on further addition of KI.

***Procedure 43b.** — To the filtrate from the $MgCl_2$ precipitate (P. 43) add 2–3 ccm. saturated oxalic acid ($H_2C_2O_4$) solution, and evaporate in a casserole to 3–4 ccm. to expel the excess of ammonia. Make the solution slightly acid with $H_2C_2O_4$, if it is not already so, add about 10 ccm. water, and digest on a steam bath for several minutes. (Purple precipitate, presence of GOLD.) To the mixture add 2–3 ccm. HCl (1.12) to dissolve any tellurium hydroxide, and filter. (Precipitate, reject; filtrate, *P. 43*c*.)

Notes. — 1. Metallic gold is precipitated readily from a solution of ammonium oxalate only when the solution is hot and slightly acid; but even under these conditions the precipitation is complete only after several minutes. If these conditions are not realized, several milligrams of gold may escape detection.

2. The more powerful reducing agents, H_2SO_3 and $SnCl_2$, also precipitate gold, but they reduce selenium and tellurium (and mercury) compounds as well.

***Procedure 43c.** — Evaporate the filtrate from the $H_2C_2O_4$ precipitate (*P. 43*b*) almost to dryness, add 10 ccm. HCl (1.12), and filter off any KCl that has separated. Collect the filtrate in a test tube, add about 0.2 gram solid Na_2SO_3, and allow the mixture to stand for at least 5 minutes, adding more Na_2SO_3 if the SO_2 odor disappears. (Red precipitate, presence of SELENIUM.) Filter. (Precipitate, reject; filtrate, *P. 43*d*.)

Notes. — 1. By the action of H_2SO_3 on selenous acid (H_2SeO_3) in the cold a voluminous red precipitate of selenium is quickly formed; but the reaction is complete only after several minutes. When the solution is hot the more compact black modification of selenium is obtained; but the test is then less delicate and less characteristic.

2. Tellurium is reduced by H_2SO_3 in moderately dilute HCl solutions, but not at all when the concentration of the acid is as great as that of specific gravity 1.12. Selenium, however, separates completely from a more concentrated acid, as well as from a more dilute one. For these reasons, though a greater concentration of HCl is unobjectionable, a lesser concentration would cause the precipitation of tellurium and obscure the selenium test.

***Procedure 43d.** — Dilute the filtrate from the H_2SO_3 precipitate (P. 43*c*) with an equal volume of water, and add a few drops of KI solution and a little solid Na_2SO_3. (Black precipitate, presence of TELLURIUM.) Filter after a few minutes. (Precipitate, reject; filtrate, *P. 43*e*.)

Notes. — 1. As stated in *P. 43*c*, N. 2, tellurium is precipitated by H_2SO_3 alone when the HCl solution of specific gravity 1.12 is diluted somewhat with water, especially if the mixture is kept hot. The precipitation, however, is much more rapid and is complete after a few minutes even in the cold if KI is also present. KI alone does not reduce tellurium compounds, but precipitates black TeI_4, which dissolves somewhat in excess of KI, forming a deep red solution of K_2TeI_6. The advantage of adding KI is that the iodine compound of tellurium is more rapidly reduced by H_2SO_3 than is the chlorine compound or tellurous acid itself.

2. Selenous acid is immediately reduced to selenium by KI in HCl solution; but this element is completely precipitated by H_2SO_3 in *P. 43*c* if the directions there given are followed; even if not so removed, it would give a red precipitate, not a black one.

3. Molybdic acid by this treatment is also slowly reduced to a lower compound, which remains in solution. Iodine may thereby be liberated and even precipitated after all the H_2SO_3 has been oxidized. For this reason the solution should not be allowed to stand for more than half an hour before filtering.

***Procedure 43e.** — Boil the filtrate from the KI precipitate (*P. 43*d*) until the SO_2 is expelled, cool the solution, add 3 or 4 ccm. 10% KCNS solution and some granulated zinc. (Red color, presence of MOLYBDENUM.) [If it is desired to form a better estimate of the quantity of molybdenum present, treat the solution as described in N. 4.]

Notes. — 1. The H_2SO_3 is boiled out, since otherwise sulphur would be precipitated by the action of zinc.

2. The red color is due to the formation of $Mo(SCN)_4$, corresponding to MoO_2, an intermediate stage in the reduction of molybdic acid (H_2MoO_4) by the zinc. The color may appear before the addition of zinc, since the H_2MoO_4 may already have been partially reduced by H_2SO_3 and HI. Long-continued action of zinc causes the red color to disappear; for the chloride $MoCl_3$, corresponding to the oxide Mo_2O_3, to which H_2MoO_4 is finally reduced, gives a colorless solution with KCNS.

3. Ferric salts also give a red color with KCNS; but a coloration arising from the presence of iron as an impurity disappears almost immediately on the addition of zinc, owing to reduction to the ferrous state.

4. It is difficult from the depth of the red coloration to form an estimate of the quantity of molybdenum present. The molybdenum may be obtained in the form of a precipitated sulphide by treating the solution to which KCNS and zinc have been added as follows: Add a little solid $KClO_3$ and boil to reoxidize the molybdenum, and finally to expel the chlorine, adding more HCl (1.20), if necessary; pass H_2S into the solution for 10 minutes, keeping it near the boiling point.

Procedure 44. — Dissolve the $MgCl_2.NH_4Cl$ precipitate (P. 43) by pouring a little HCl (1.12) through the filter, heat the solution obtained nearly to boiling, and pass in H_2S for at least 5 minutes, keeping the solution hot. (White precipitate turning yellow, presence of ARSENIC.) (Precipitate and solution, reject.)

Notes. — 1. The slow formation in a dilute acid solution of a pale yellow precipitate with H_2S is a characteristic test for H_3AsO_4. The precipitate is a mixture of As_2S_5, As_2S_3, and sulphur, the amount of As_2S_5 being comparatively small in the presence of strong HCl and at high temperatures.

2. A considerable amount of H_2S may be absorbed by a dilute H_3AsO_4 solution before any precipitate appears. This is due to the formation of H_3AsO_3S, which then decomposes slowly, giving H_3AsO_3 and sulphur. This last decomposition may be accelerated by increasing the H^+ concentration and by raising the temperature. The H_3AsO_3 formed reacts at once with H_2S, and As_2S_3 is precipitated. The reactions taking place are, therefore,

$$H_3AsO_4 + H_2S = H_3AsO_3S + H_2O,$$
$$H_3AsO_3S = H_3AsO_3 + S,$$
$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O,$$

which together give the reaction,

$$2H_3AsO_4 + 5H_2S = As_2S_3 + S_2 + 8H_2O.$$

The rate of this reaction depends upon the rate of the slowest of the single reactions — the decomposition of H_3AsO_3S. As_2S_5 is produced by an independent reaction,

$$2H_3AsO_4 + 5H_2S = As_2S_5 + 4H_2O,$$

which takes place very slowly.

Procedure 45. — Heat the solution of the sulphides (P. 42), which should contain 10 ccm. HCl (1.20) in a total volume of 50 ccm., to

about 90°, and pass in H_2S gas for about 5 minutes, keeping the solution at about 90°. If no precipitate appears, add about 5 ccm water, and again saturate with H_2S at the same temperature as before. (Orange red precipitate, presence of ANTIMONY.) Filter while hot, add 5 ccm. water, heat the filtrate nearly to boiling, again saturate with H_2S to ensure complete precipitation of antimony, and filter if any precipitate forms. Wash the precipitates with hot water. (Precipitate, P. 46; filtrate, P. 47.)

Notes. — 1. By following carefully the directions given in P. 42 and this procedure, a good separation of antimony and tin may be obtained; when only 1 mgm. of antimony is present it is precipitated as Sb_2S_3, while even 500 mgm. of (stannic) tin give no precipitate. If, however, the HCl solution be too concentrated, a small quantity of antimony will escape detection; hence the precaution of adding a little water to the solution and repeating the treatment with H_2S. If the HCl solution be too dilute, or if it be not kept hot, some SnS_2 may precipitate when a large amount of tin is present. When mixed with a little Sb_2S_3 a brown precipitate results.

2. If mercury or copper be present in the substance and ammonium polysulphide has been used, HgS or CuS may be precipitated at this point as a gray or black precipitate.

Procedure 46. — Dissolve the H_2S precipitate (P. 45) in a little strong HCl in a small casserole and evaporate the solution to about 1 ccm. Introduce beneath the solution a piece of platinum foil and place upon it a piece of pure tin. After several minutes wash carefully with water and cover the platinum foil with (alkaline) NaOCl solution. (Black deposit on the platinum undissolved by NaOCl, presence of ANTIMONY.) (Precipitate and solution, reject.)

Notes. — 1. Mercury and copper, if present, will also be precipitated in the metallic condition upon the platinum, but the antimony may be easily distinguished from them by its black color. Tin is used rather than zinc in precipitating the antimony, since zinc would also precipitate tin from the solution.

2. The treatment with NaOCl serves to prove that the black precipitate does not consist of arsenic or tellurium; for these elements are readily dissolved by it, while antimony is not. Since, however, several milligrams of arsenic must be present before the treatment with tin would give a deposit on the platinum, an arsenic deposit will probably never be obtained in an actual analysis.

Procedure 47. — Cool the filtrate from the H_2S precipitate (P. 45), dilute with 20 ccm. water, and pass in H_2S for 10 minutes. (Yellow precipitate, presence of TIN.) If there is a precipitate, evaporate the mixture without filtering to 5–10 ccm., add about 1 gram of granulated zinc, and allow the action to continue for several minutes, but not until all the zinc is dissolved. (Gray, spongy precipitate, presence of TIN.) Decant the solution into a test tube, allow any particles suspended in it to settle out, decant again, and unite the two residues. Heat the residues with 2–5 ccm. HCl (1.20) until everything (except any particles of carbon) is dissolved. Dilute the solution with one-half its volume of water, and pour it at once through a small filter into 5 ccm. $HgCl_2$ solution. (White precipitate, presence of TIN.)

Notes. — 1. The solution is precipitated with H_2S in the cold, because a small quantity of SnS_2 would not separate from a hot solution unless the acid were more diluted. The addition of much water is avoided, since it has to be evaporated off in the confirmatory test.

2. In the confirmatory test the precipitate of SnS_2 is not filtered off, but is dissolved by concentrating the acid by evaporation, since it clogs the filter and tends to pass through it. The zinc must not be allowed to dissolve entirely, since the tin might then also dissolve. Care must also be taken not to lose it in the process of decantation or by failing to dissolve it completely. Finally, since $SnCl_2$ oxidizes rapidly in the air, the solution in HCl must be immediately added to the $HgCl_2$ solution. If these precautions are observed, the presence of half a milligram of tin in the HCl solution of the sulphides (P. 4) may be detected after some practice. The confirmatory test is, however, less delicate than the precipitation by H_2S, but it is more characteristic, since $SbCl_3$, even if present, does not reduce $HgCl_2$.

TEST ANALYSES

Numerous analyses were made to test the efficiency of the process above described. Nearly all of those which were made after the procedure assumed final form are reproduced in the tables below. In these tables the numbers in each vertical column show the weights in milligrams of the various elements which the solution submitted to analysis contained. The results of the tests for each element are shown by the letters following these numbers. That the result was satisfactory is indicated by the letter S; that is, when the element was present, that the test for it, however small, was unmistakable, and therefore conclu-

sive; and when the element was absent, that a good blank test was obtained. When the test was very small, especially in comparison to the quantity of the element present, though still unmistakable, this is sometimes indicated by the symbol S—. When in the presence of the element the test failed, or in its absence a result was obtained that might be thought to indicate its presence, the letter F is used. When the result was doubtful or inconclusive, owing to the appearance or small size of the precipitate, this is indicated by the letter D. When the test was not tried, if the element was present, a dash is used in place of a letter; or, if the element was not present, dots are inserted.

Silver Group

All these analyses (Nos. 1–9) were begun at P. 11 and carried through P. 15.

T. A. No.	1	2	3	4	5, 6	7	8	9
Pb	500 S	500	. .	. .	. .	. .	. .	. .
Ag	0 S	1 S	500 S	500 S	0 S	1 F	1 S—	2 S
Hg	0 S	1 S	0 S	1 S	500 S	500 S	500 S	500 S

Copper Group

The following analyses (Nos. 10–20) were begun at P. 21 and were carried through P. 23–30, P. 22 being omitted. In addition, tin was tested for by P. 25, 41, 42, 45, and 47.

T. A. No.	10	11	12	13	14	15
Hg	500 S	500 S	500 S	500 S	1 S—	0 S
Sn (ous)	0 S	2 F	4 S	2 S—, F[1]	2 S—, F[1]	0 S
Pb	0 S	1 S—	1 F	2 S	1 S	0 S
Bi	0 S	1 S	1 S	0 S	500 S	500 S
Cu	0 S	1 S	1 S	0 S	1 S	0 S
Cd	0 S	1 S	1 S	0 D[2]	1 S	0 S

T. A. No.	16	17	18	19	20
Hg	0 S	1 S	0 S	1 S	2 S
Sn (ous)	0 S	2 S	0 S	2 S	0 S
Pb	0 S	1 S	0 S	1 F	1 S
Bi	0 S	1 S	0 S	1 S	1 S
Cu	500 S	500 S	0 S	1 S	1 S
Cd	0 D[2]	1 S	500 S	500 S	500 S

The following analyses (Nos. 21–28) were begun at P. 21, the H_2S precipitate was digested once with 10 ccm. ammonium polysulphide (P. 22), and the residue analyzed by P. 23–30.

T. A. No.	21	22	23	24	25	26	27	28
Hg (ic)	2 S	1 D	. .	. .	. .	. .	. .	. .
Cu	. .	. .	2 S—[3]	5 S	3 S	2 S	2 S[3]	3 S
Bi	. .	. .	. .	. .	. .	500 S	. .	. .
Sn (ous) . . .	. .	. .	300 S	300	300	. .	50 S	. .
Sb (ous) . . .	300 S	300 S	. .	. .	. .	. .	. .	200 S

The following analyses (Nos. 29–30) were made in the same way, except that 25 ccm. ammonium monosulphide were used.

T. A. No.	29	30
Hg (ic)	1 S	1 S
Cu	1 S[5]	1 F
Sb (ic)	300 —	. .
As	. .	250 —
Sn (ic)	. .	250 —

Tin Group

In the following analyses (Nos. 31–56) the substances were dissolved directly in ammonium polysulphide and the solution treated by P. 41–47.

T. A. No.	31	32, 33	34, 35, 36	37, 38	39, 40	41, 42, 43	44, 45	46	47
As . . .	0 S	2 S	1 S	500 S	. .	. .	. .	. .	. .
Sb . . .	500 S	500 S	500 S	0 S	0 S	1 S	500 S	500 S	500 S
Sn . . .	. .	. .	. .	0 S	500 S	500 S	0 S	1 S—[6]	1 S

T. A. No.	48	49	50	51	52	53, 54	55	56
As	0 S	1 S	. .	2 S	1 S	500 S	500 S	500 S
Sb	0 S	1 S	1 S	2 S	200 S	1 S	1 S	0 S
Sn . . .	500 S	500 S	1 S	2 S	500 S	1 S	1 S—, F[1]	1 S

In the following experiments (Nos. 57–90), in which a large quantity of an element of the copper group was present with the tin group, the analysis was begun at P. 21, the H_2S precipitate was treated once with 10 ccm. ammonium polysulphide, and the solution analyzed by P. 41–47. The copper-group residue was not treated by P. 23–25 to recover tin.

T. A. No.	57	58	59	60	61	62
Bi	500 —	500 —	500 —	500 —	500 —	500 —
As	0 S[7]	1 F	2 S	1 S	. .	. .
Sb (ous)	0 S	1 S	2 S	0 S	. .	. .
Sn (ous)	0 S	1 F	2 S	0 S	2 S	1 S[8]

T. A. No.	63	64	65	66	67	68
Hg	500	500 —	500 —	500 —	500 —	500 —
As	0 S[7]	1 S	2 S	0 —	. .	. .
Sb (ous)	0 S	1 S	2 S	0 S	. .	. .
Sn (ic)	0 S	1 F	2 F	5 F	5 F	10 S[9]

T. A. No.	69	70	71	72	73	74	75
Cu	500 —	500 —	500 —	500 —	500 —	500 —	500 —
As	0 S[7]	1 S	2 S	0 S	. .	. .	. .
Sb (ous)	0 S	1 S	2 S	0 S	. .	. .	. .
Sn (ous)	0 S	1 F	2 F	2 F	4 S—, F[1]	5 S[9]	3 S—, F[1] (stannic)

T. A. No.	76	77	78	79, 80	81	82	83	84
Cd . . .	500 —	500 —	500 —	500 —	500 —	500 —	500 —	500 —
As . . .	0 S	2 S	1 S	1 S	0 S	. .	. .	. .
Sb (ous)	0 S	2 S	1 S	1 S	0 S	. .	. .	. .
Sn (ous)	0 S	2 F	0 S	2 F	10 F	10 S—, F[1]	15 S[8]	15 S—, F[1]
Sn (ic) .	0 S	. .	. .	. .	. .	. .	. .	. .

T. A. No.	85	86	87, 88	89	90
Cd	500 —	500 —	500 —	500 —	500 —
As	. .	. .	. .	. .	. .
Sb (ous)	. .	. .	. .	. .	. .
Sn (ous)	20 S[9]	25 S—, F[1]	25 S	. .	. .
Sn (ic)	. .	. .	. .	3 F	5 S[9]

The following analyses (Nos. 91–97) were made by Mr. A. L. Smith in the same way as the preceding ones, except that 25 ccm. ammonium monosulphide, instead of 10 ccm. polysulphide, were used in digesting the H_2S precipitate.

A. T. No.	91	92	93	94	95	96	97
Hg (ic)	. .	. .	. .	. .	. .	. .	500 —
Bi	500 —	500 —	. .	. .	500 —	. .	. .
Cd	. .	. .	. .	500 —	. .	250 —	. .
Cu	. .	. .	500 —	. .	. .	250 —	. .
As (ic)	. .	. .	. .	. .	. .	. .	1 S
Sb (ic)	2 S	4 S	2 S	2 S	1 S	1 S	1 S
Sn (ic)	5 F[12]	10 F[12]	5 S	5 S	5 F[12]	5 F[12]	5 F[12 13]

In the following analyses (Nos. 98–100), also made by Mr. A. L. Smith, the solution in ammonium monosulphide and the residue were treated separately in order to detect tin. It was not detected in any case in the analysis of the solution. The results shown in the table were obtained in the analysis of the residue.

T. A. No.	98	99	100
Hg (ic)	250 —	250 —	. .
Bi	250 —	250 —	. .
Cd	. .	. .	250 —
Cu	. .	. .	250 —
Sn (ic)	2 F	5 S	3 S—, F[1]

Mixtures Containing the Rarer Elements

The following analyses were made, starting at P. 41, with an ammonium polysulphide solution, and following P. 42, 43, and *P. 43*a*–43*c*.

T. A. No.	101	102	103	104	105
As	. .	. .	300 S	200 S	200 S
Sb	. .	. .	200 —	. .	. .
Sn	. .	. .	200 —	200 —	200 —
Se	0 S	1 S	1 S	1 S	0.5 S
Te	0 S	1 S	1 —	2 S	1 S
Mo	100 S	50 S	1 S	0 S	0.5 S

The following analyses were begun at P. 21, the H_2S precipitate was extracted with ammonium polysulphide (P. 22), the solution was analyzed by P. 41–43 and *P. 43*a*–43*c*, and the residue treated by P. 23, 24, and *P. 24*a*.

T. A. No.	106	107	108
Cu	300 —	200 —	100 —
Hg	0 S	0 S	0 S
Pt	5 S[11]	3 S[10]	2 S[10]
Au	5 S[10]	3 S[10]	1 S[11]
Te	. .	. .	10 S

The following analyses (Nos. 109–111) were made by Mr. A. L. Smith, beginning with P. 21 and following through the whole process as described in P. 21–47. Ammonium monosulphide was used in separating the copper and tin groups.

T. A. No.	109	110	111	112[18]	113
Hg (ic)	1 D[14]	1 —	1 F[14]	. .	2 D[14]
Pb	1 F	1 S	1 S—	. .	1 S
Bi	0 S	1 S[19]	1 S[19]	. .	1 S
Cd	1 D	1	1 F[16]	1 S	2 S
Cu	1 S	1 S	1 S	. .	1 S
As (ic)	1 F	1 S	1 S	. .	1 S
Sb (ic)	0 S	1 S	1 S—	1 S	1 S
Sn (ic)	2 S	1 S—, F[1]	1 S—, F[1]	. .	2 S
Ft	1 S[15]	1 S[20]	1 S	. .	1 S[15]
Au	1 S[15]	1 S[20]	1 S[15]	. .	1 S[15]
Se	1 F	1 F[21]	1 S—	1 S	2 F[21]
Te	1 F	1 F	1 S—[17]	1 S	2 F[22]
Mo	1 D	1 D	1 S—[17]	1 S	2 S

[1] The confirmatory test with $HgCl_2$ failed, but a distinct precipitate of SnS_2 was obtained.

[2] A very small, dark precipitate was obtained.

[3] No blue color was produced with NH_4OH, but a slight pink precipitate with $K_4Fe(CN)_6$ was visible on the filter.

[4] A good blue color was obtained with NH_4OH, showing that a small quantity of copper is not dissolved out of a large copper-group precipitate by the polysulphide.

[5] No blue color could be seen, but a very distinct pink precipitate formed with $K_4Fe(CN)_6$.

[6] In this analysis the confirmatory tin test failed, but this was doubtless due to the fact that the SnS_2 precipitate was filtered off and dissolved in HCl, instead of evaporating the mixture as usual.

[7] The HCl precipitate from the polysulphide solution was very light-colored, or, if not, when it was extracted with NH_4OH the solution gave no precipitate with HCl; so the analysis was not carried further.

[8] A fair SnS_2 precipitate was produced, but owing to an accident the confirmatory test was not tried.

[9] The SnS_2 precipitate produced in P. 47 was estimated to contain only 1–3 mgm. Sn.

[10] In these analyses the moist H_2S precipitate was left on the filter for several hours before treating with ammonium polysulphide.

[11] Satisfactory tests were obtained for gold and for platinum both in the copper and tin groups; and the final precipitates were not far from equal in size.

[12] No precipitate of SnS_2 was produced in P. 47.

[13] The residue undissolved by ammonium sulphide was treated by P. 23, 24, 25, 41, and 42, and the HCl solution so obtained reduced directly with Zn, the residue dissolved, and $HgCl_2$ added; but no test for tin was obtained.

[14] A black precipitate was produced in the test with $SnCl_2$, probably due to the presence of gold. It was treated with hot HNO_3 (1.20), and it did not dissolve, showing it was not wholly mercury; the solution after evaporation with HCl was tested with $SnCl_2$, but only an inconclusive turbidity was obtained.

[15] Tests for these elements were obtained in the analyses of both the copper and tin groups.

[16] All or nearly all the cadmium failed to be precipitated by H_2S from the 100 ccm. of solution containing 4 ccm. HCl (1.12), even though the gas was passed in for 10 minutes; for it was recovered from the filtrate by adding 50 ccm. more water and passing in H_2S for 10 minutes, and then confirmed by P. 23, 27, and 30.

[17] Nearly all the tellurium and molybdenum failed to be precipitated by H_2S; for they were recovered from the filtrate by adding NH_4OH and NH_4SH and acidifying, and were detected by treating the precipitate by P. 43, *43*a*, *43*c*, *43*d*, and *43*e*.

[18] In T. A. No. 112 the last part of P. 43 and *P. 43*b* were omitted.

[19] No distinct turbidity was visible, but upon filtering and treating with sodium stannite the filter was much darkened.

[20] Tests for these elements were obtained only in the analysis of the tin group.

[21] A red precipitate separated in the lead test upon evaporating with H_2SO_4, which was probably selenium, and indicated that it had not been dissolved out by $(NH_4)_2S$.

[22] In testing for arsenic with $MgCl_2$ a flocculent precipitate accompanied the crystalline one of $MgNH_4AsO_4$, and on dissolving this in HCl and adding H_2S a black precipitate resulted. This was dissolved in HCl and $KClO_3$ and treated by *P. 24*d*: a black precipitate resulted, showing that tellurium was precipitated with the arsenic.

The test analyses of the silver group (Nos. 1–9) show that 1 mgm. of mercurous mercury is detected in the presence of 500 mgm. of either lead or silver; and that 1 mgm. of silver is detected without difficulty in the presence of 500 mgm. of lead, but that in the presence of 500 mgm. of mercury 1 mgm. of silver lies at about the limit of detectability.

The test analyses of the copper group (Nos. 10–20) show (at any rate when the ammonium sulphide treatment is omitted) that even 1 mgm. of mercury, bismuth, copper, or cadmium is detected in the presence of 500 mgm. of any other one of these elements; that with lead in presence of 500 mgm. of any one of these elements 1 mgm. is near the limit, probably owing to the difficulty of securing complete precipitation with H_2S; and that with stannous tin the limit of detectability is at 2 mgm. The blank tests were satisfactory in all cases, except that a very small, dark precipitate was sometimes obtained in the cadmium test with H_2S. Even when the H_2S precipitate was treated

with ammonium polysulphide (T. A. Nos. 21–28), which dissolves some copper and mercury, these elements were detected in all cases where 2 mgm. were present; and when monosulphide was used (as in T. A. Nos. 29–30) 1 mgm. of mercury was twice detected, while with copper it was found in one analysis and lost in the other.

The test analyses of the tin group in which the copper group was not present, which were begun with an ammonium polysulphide solution of the elements (Nos. 31–56), show that 1 mgm. of arsenic, antimony, or tin is invariably detected, even in the presence of 500 mgm. of any other one of these elements.

The test analyses in which the elements of the tin group were associated with 500 mgm. of an element of the copper group and in which the H_2S precipitate was treated with ammonium polysulphide (Nos. 57–90) show that 1 mgm. of arsenic or antimony is almost always detected; but that a much larger quantity of tin in some combinations is not detected, if only the ammonium sulphide solution is analyzed for it. Thus, while in the presence of bismuth 1 to 2 mgm. of stannous tin were found, yet in the presence of copper 4 to 5 mgm., and in that of cadmium 10–15 mgm. of it were lost; and 3 to 5 mgm. of stannic tin were lost in the presence of mercury or cadmium.

In the analyses in which ammonium monosulphide was used (Nos. 91–97), the detection of antimony in the higher state of oxidation and of arsenic is nearly as satisfactory, 1 or 2 mgm. having been always found; but a larger quantity of stannic tin remains with the copper group than when the polysulphide is used, 5 mgm. being retained even by bismuth.

These results clearly show the necessity of testing for tin in the analysis of the copper as well as of the tin group, and T. A. Nos. 98–100 show that it can be detected in the copper group analyses when 3 mgm. are present.

In the test analyses with mixtures containing the rarer elements (Nos. 101–113) 1 mgm. of platinum or gold was always detected; and the same was true of 1 mgm. of selenium, tellurium, and molybdenum in the analyses that started at the beginning of the tin group, but not in those where elements of the copper group were present and the analysis was begun with the H_2S precipitation.

Confirmatory Experiments and References

Analysis of the Silver Group

P. 11, N. 1: Solubility of $PbCl_2$ and TlCl in Water and in HCl. — See Noyes, *Z. phys. Chem.*, **9**, 614, 623 (1892); Engel, *Ann. chim. phys.*, (6) **17**, 359 (1889); Ditte, *Compt. rend.*, **92**, 718 (1881).

P. 13, N. 1: Solubility of $PbSO_4$. — See C. E., P. 26, N. 1.

**P. 13a, N. 1: Test for Thallium with KI.* — To 50 mgm. Pb as $PbCl_2$, dissolved in 20 ccm. water, 5 ccm. H_2SO_4 (1.84) were added; the mixture was cooled and filtered, and to the filtrate a few drops KI solution were added: no precipitate appeared.—The experiment was repeated, except that 1 mgm. Tl as Tl_2SO_4 was also present: a pale yellow precipitate of TlI resulted.

To solutions containing 0.5 mgm. Tl as Tl_2SO_4 and 4 ccm. HCl (1.12) and 10 ccm. or 20 ccm. water, respectively, a few drops of a normal KI solution were added: a yellow precipitate separated in the first experiment, but only a faint yellow turbidity appeared in the second.

**P. 13a, N. 2: Oxidation of Thallous Salts.* — 100 mgm. Tl as Tl_2SO_4 were dissolved in 10 ccm. HNO_3 (1.42) and evaporated to about 2 ccm.; the solution was diluted to 20 ccm. and 1–2 ccm. HCl (1.12) added: a large light-yellow precipitate separated, thus showing that some, but not much, of the thallium had been oxidized.

100 mgm. Tl as Tl_2SO_4 were dissolved in 2 ccm. HNO_3 (1.42) and about 5 ccm. HCl (1.20) were added: a white precipitate separated at first, but dissolved on warming. The mixture was evaporated to about 2 ccm., cooled, and diluted to 20 ccm.: no precipitate separated, even when a little HCl was added, thus showing that the thallium was in the thallic state. — The experiment was repeated, except that the *aqua regia* solution was evaporated to dryness and the residue dried by heating slightly; to it 4 ccm. HCl (1.12) and 20 ccm. water were added: a large light-yellow precipitate separated, showing that the thallic salt had been largely but not completely reduced.

P. 14, N. 1: Explanation of the Solubility of $PbSO_4$ in Ammonium Acetate Solution. — See Noyes and Whitcomb, *J. Am. Chem. Soc.*, **27**, 747 (1905).

P. 14, N. 2: Behavior of Bismuth Compounds towards Ammonium Acetate and K_2CrO_4. — 5 mgm. Bi as solid bismuth oxysulphate (see P. 26, N. 5) were treated by P. 14, 20 ccm. normal ammonium acetate and 5 ccm. 5-normal acetic acid being used: a yellow precipitate very similar in appearance to $PbCrO_4$ was formed on the addition of K_2CrO_4, but this dissolved quickly in the acetic acid. — The experiment was repeated with 1 mgm. Bi as nitrate: the result was the same.

P. 15, N. 1: Molecular Formula of Gaseous Mercurous Chloride. —

Baker (*J. Chem. Soc. Trans.*, 77, 646. 1900) has shown that absolutely dry mercurous chloride vapor has a density corresponding to the formula Hg_2Cl_2.

Condition of Mercurous Salts in Solution. — See Ogg, *Z. phys. Chem.*, **27**, 290–299 (1898); Abel, *Z. anorg. Chem.*, **26**, 377 (1901).

Action of NH_4OH on Hg_2Cl_2. — For the evidence that the black residue is a mixture of Hg and $HgClNH_2$, see Barfoed, *J. prakt. Chem.*, **39**, 201 (1889); Pesci, *Gazz. chim. ital.*, **21**, 569 (1891); and Sen, *Z. anorg. Chem.*, **33**, 197 (1903).

P. 15, N. 3: Complex Silver-Ammonia Anions. — See Bodländer and Fittig, *Z. phys. Chem.*, **39**, 597 (1902); Whitney and Melcher, *J. Am. Chem. Soc.*, **25**, 69 (1903); Bodländer and Eberlein, *Z. anorg. Chem.*, **39**, 197 (1904); Lucas, *Z. anorg. Chem.*, **41**, 193 (1904).

P. 15, N. 5: Solubility of AgCl in Chloride Solutions. — See Comey, *Dictionary of Solubilities*, p. 373.

1 mgm. Ag as AgCl was dissolved in 5 ccm. NH_4OH (0.96), the solution obtained was made acid with HCl: no precipitate separated. — The experiment was repeated, using HNO_3 instead of HCl: a precipitate formed. — 5 mgm. Ag as AgCl were dissolved in 15 ccm. NH_4OH (0.96), and the solution made acid with HCl: no precipitate separated. An equal volume of water was added: AgCl precipitated.

Precipitation and Separation of the Copper and Tin Groups

P. 21, N. 1: Order of Precipitation of the Sulphides of the Copper and Tin Groups from Cold HCl Solution. — 2 mgm. As as As_2O_3, 2 mgm. Hg, and 2 mgm. Cu, each as chloride, were in separate experiments dissolved in 2 ccm. HCl (1.20), and 2 mgm. of each of the elements of the copper and tin groups were in separate experiments dissolved in 4 ccm. HCl (1.12); each solution was put into a small bottle, saturated completely with H_2S at room temperature, the bottle corked, and allowed to stand 15 minutes. In cases where no precipitate formed the solution was successively diluted with measured quantities of water, being again saturated with H_2S and allowed to stand after each addition: the most strongly acid solution from which each element separated is shown by the following table:

Ccm. HCl (1.20)	2	. .	. .	. .	. .	. .
Ccm. HCl (1.12)	. .	4	4	4	4	4
Ccm. water	0	0	4	12	44	96
Elements precipitated	As	Hg, Cu	Sb	Bi, Sn (ic)	Cd	Pb, Sn (ous)

The cadmium, lead, and stannous sulphides precipitated slightly and only after several minutes; the others almost at once.

Order of Precipitation of the Sulphides of the Iron Group from Weak Acid Solutions. — 50 mgm. Zn and 500 mgm. Zn as nitrate, 500 mgm. Fe (ous), 500 mgm. Ni, 500 mgm. Co, and 500 mgm. Mn as sulphate were in separate experiments dissolved in 1 ccm. HCl (1.12) and 100 ccm. water, saturated with H_2S at room temperature, and allowed to stand 10 minutes: zinc was precipitated from both its solutions, but none of the other elements. — The experiments with 50 mgm. Zn and 500 mgm. Zn were repeated, except that 2 ccm. HCl (1.12) was used: ZnS precipitated after several minutes in the 500 mgm. portion, but not in the 50 mgm. one.

500 mgm. each of ferrous Fe, Co, Ni, and Mn as sulphate were dissolved in 100 ccm. water and saturated at room temperature with H_2S for 10 minutes: FeS slowly precipitated in considerable quantity, but none of the other sulphides. — The experiment was repeated, except that the substances were dissolved in 10 ccm. 10% acetic acid solution, 1 ccm. 10% $NaC_2H_3O_2$ solution, and 90 ccm. water: the result was the same. The last experiment was repeated, except that 10 ccm. instead of 1 ccm. $NaC_2H_3O_2$ solution were used: large quantities of NiS and CoS as well as of FeS precipitated, but no MnS. — In another experiment 500 mgm. Mn as $MnSO_4$ were dissolved in 1 ccm. 10% $HC_2H_3O_2$ solution, 10 ccm. 10% $NaC_2H_3O_2$ solution, and 90 ccm. water, and saturated with H_2S: no MnS precipitated.

P. 21, N. 3: Precipitation of Arsenic, Platinum, and Molybdenum by H_2S. — 100 mgm. As as H_3AsO_4, 100 mgm. Mo as H_2MoO_4, and 25 mgm. Pt as H_2PtCl_6 were dissolved in separate 100 ccm. portions of dilute HCl (one volume HCl (1.12) to twenty-five volumes water) and were saturated with H_2S in the cold: less than 1 mgm. of As and of Pt, but considerable Mo, precipitated as sulphides in 10 minutes. The three solutions were then filtered, heated to boiling, and saturated with H_2S at that temperature for about 15 minutes: a large precipitate resulted in each case. The solutions were filtered, saturated in the cold with H_2S, and heated in pressure bottles in the steam bath for 1 hour: a considerable precipitate separated from each solution, estimated to contain about 5 mgm. As in the arsenic solution and 10 mgm. Mo in the molybdenum solution.

100 mgm. As as H_3AsO_4 were added to 100 ccm. HCl (1.20) and saturated in the cold with H_2S: a large yellow precipitate separated. After 5 minutes the mixture was diluted with half its volume of water and filtered; the filtrate was heated to 100° and H_2S passed in for 10 minutes: a small precipitate estimated to contain only 3–5 mgm. As resulted. These two experiments with arsenic acid show that the precipitation takes place much more rapidly in the presence of concentrated HCl.

Precipitation of Cadmium and Lead by H_2S. — Separate solutions contain-

ing 5 mgm. Cd, 5 mgm. Pb, 10 mgm. Cd, and 10 mgm. Pb, respectively, in 100 ccm. of a mixture of one volume HCl (1.12) and fifteen volumes water were saturated in the cold with H_2S for 15 minutes: precipitates began to form only after 10 or 15 minutes in each of the solutions.

Separate solutions containing 1 mgm. Cd and 1 mgm. Pb in 100 ccm. of a mixture of one volume HCl (1.12) and twenty-five volumes water were saturated in the cold with H_2S: both solutions showed precipitates, but that in the case of lead was scarcely visible until it was collected on a filter. The PbS was filtered out and NH_4OH and $(NH_4)_2S$ added to the filtrate: a brown color corresponding to 0.1–0.2 mgm. Pb resulted, showing that substantially all the lead was precipitated.

Precipitation of Zinc by H_2S. — Solutions containing 500 mgm. Zn in three 100 ccm. portions of dilute HCl, containing one volume HCl (1.12) to twenty-five volumes water, to forty volumes water, and to fifty volumes water, respectively, were saturated in the cold with H_2S, then heated to boiling, and again saturated with H_2S: in the cold, H_2S failed to produce a precipitate in any of the solutions in 5 minutes; but on heating, a slight precipitate formed in the 1 : 40, and a heavy one in the 1 : 50, but none in the 1 : 25 mixture.

Precipitation of Titanium Hydroxide by Hydrolysis. — Separate 100 mgm. portions of Ti in 100 ccm. dilute HCl, containing one volume HCl (1.12) to twenty volumes water, to ten volumes water, and to eight volumes water, respectively, were saturated cold with H_2S and then heated in pressure bottles in a steam bath for 2 hours: in the 1 : 20 volume solution a very large white precipitate had formed in 30 minutes; the 1 : 10 solution remained clear for 45 minutes, and then showed only a turbidity; and the 1 : 8 solution remained unchanged during the 2 hours.

Precipitation of Bismuth and Antimony Oxychlorides by Water. — Separate solutions containing 500 mgm. Bi as nitrate, 400 mgm. Sb as $SbCl_3$, and 300 mgm. Sb as Sb_2O_5 (obtained by evaporating an $SbCl_3$ solution with *aqua regia*) were evaporated with HCl almost to dryness; 4 ccm. HCl (1.12) and 36 ccm. water were added, and the mixture was heated: from the bismuth solution no precipitate separated either in the cold or upon heating; in the antimonous solution a large white precipitate formed in the cold, but dissolved almost completely upon heating; and in the antimonic solution a large precipitate separated in the cold and did not appear to dissolve upon heating. To the bismuth solution 20 ccm. more water were added: a white precipitate then began to form.

P. 21, N. 3: Separation of the Copper and Tin Groups from the Iron Group by H_2S. — Mixtures of elements as shown below were dissolved in 4 ccm. HCl (1.12) and 36 ccm. water and treated exactly as described in P. 21, except that the solutions containing cadmium were diluted at once

to 100 ccm. and saturated at room temperature with H_2S; the solutions were filtered after 10–30 minutes, the filtrate boiled to expel H_2S, HNO_3 added, the mixture again boiled, NH_4OH added to detect iron, any precipitate filtered off, and H_2S was passed into the filtrate or $(NH_4)_2S$ was added to it to detect zinc, nickel, or cobalt: the results are recorded below as in the Test Analyses:

Cd	500 —	500 —	500 —	500 —	500 —
Zn	0 S	2 S	1 S[1]	. .	. .
Fe	0 S	. .	. .	2 S	1 S
Ni	0 S	. .	. .	. .	1 S
Cu	500 —	500 —	. .	. .	. .
Bi	. .	. .	200 —	200 —	. .
As (ous)	. .	. .	100 —	100 —	. .
Sb (ous)	. .	. .	100 —	100 —	. .
Sn (ic)	. .	. .	200 —	200 —	. .
Zn	. .	. .	1 S[1]	. .	. .
Fe	1 S	0 S	. .	. .	. .
Ni	1 S	. .	. .	1 S	. .
Co	. .	1 S[2]	. .	. .	. .

[1] A nearly white precipitate was obtained with $(NH_4)_2S$.

[2] The black $(NH_4)_2S$ precipitate was dissolved in *aqua regia* and the solution evaporated just to dryness: the residue had a slight pink color.

P. 21, N. 4: Composition of the H_2S Precipitates. — From solution of $HgCl_2$ in excess, see Rose, *Pogg. Ann.*, **13**, 64 (1828). From arsenic acid solutions, see C. E., P. 44, N. 1, 2, and 3. From antimonic solutions, see Klenker, *J. prakt. Chem.*, **59**, 150 (1899). From chloroplatinic acid, see Antony and Lucchesi, *Gazz. chim. ital.*, **26**, 211 (1896). From gold chloride, see Hoffmann and Krüss, *Ber. d. chem. Ges.*, **20**, 2369, 2704 (1887). From selenous acid, see Ditte, *Compt. rend.*, **73**, 625, 660 (1871); Divers and Shimidzu, *J. Chem. Soc.*, **47**, 441 (1885). From tellurous acid, see Becker, *Liebig's Ann. Chem.*, **180**, 260 (1875).

P. 21, N. 5: Action of HNO_3 on H_2S. — Separate 50 ccm. portions of mixtures of one volume of HNO_3 (1.20) in 2.5, 5, 10, and 20 volumes of solution were heated to boiling and saturated with H_2S at that temperature: in the first solution a precipitate of sulphur soon appeared, in the

second a slight precipitate formed after 10 minutes, and in the last two no precipitates formed in 20 minutes.

P. 22, N. 1: Solubility of SnS and Sb_2S_3 in Ammonium Monosulphide. — See C. E., P. 22, N. 4.

P. 22, N. 2: Hydrolysis of the Alkaline Sulphides and Composition of the Polysulphides. — It has been shown by C. F. Sammet (*Thesis, M. I. T.*, 1903) that a solution of the empirical composition $(NH_4)_2S$ containing 0.1 formula weight per liter is practically completely hydrolyzed into NH_4OH and NH_4SH, and that in the same solution the latter is only slightly (roughly, 0.3%) hydrolyzed into H_2S and a second equivalent of NH_4OH. But in a solution containing only half as much NH_4OH, *i. e.*, in a solution containing 0.1 formula weight NH_4SH per liter, the degree of hydrolysis increases to several per cent.

Küster and Heberlein (*Z. anorg. Chem.*, **43**, 71. 1905) have found Na_2S in a solution containing 0.05 formula weights per liter to be 86% hydrolyzed into NaOH and NaSH, and NaSH in 0.01 normal solution to be only 0.15% hydrolyzed into NaOH and H_2S. For the degree of hydrolysis of NaSH, Walker (*Z. phys. Chem.*, **32**, 137. 1900) found practically the same value by an independent method.

Küster and Heberlein also investigated the hydrolysis of the polysulphides of sodium, and showed that the degree of hydrolysis decreases with increasing sulphur-content; thus a solution of the composition Na_2S_2 was 65%, a solution of Na_2S_4, only 12% hydrolyzed. They found further that Na_2S solutions of the following concentrations when saturated with sulphur at 24° have the empirical composition Na_2S_x where x has the following values:

Formula weights Na_2S per liter	2.0	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{32}$
Value of x	4.48	4.84	5.12	5.24

It was found that x varied only slightly with the temperature. According to these authors, Na_2S_4, and less readily Na_2S_5, have been obtained in the solid form by evaporating aqueous solutions; but Na_2S_2 and Na_2S_3 have not been so obtained. All of these have, however, been crystallized from alcoholic solutions (H. Boettger, *Liebig's Ann. Chem.*, **223**, 335. 1884; H. Rebs, *Liebig's Ann. Chem.*, **246**, 358. 1888).

Bloxam (*J. Chem. Soc.*, **67**, 300. 1894; **77**, 753. 1900) found that a very concentrated ammonium sulphide solution prepared from NH_4OH (0.88) so as to have exactly the composition $(NH_4)_2S$ dissolved sulphur until the composition became approximately $(NH_4)_2S_{4.5}$. He has obtained under various special conditions the following solid salts: $(NH_4)_2S_4$, $(NH_4)_2S_5$, $(NH_4)_2S_7$, $(NH_4)_2S_9$, $(NH_4)_4S_7$, and $(NH_4)_4S_9$; Na_2S, NaSH, Na_2S_5, and Na_4S_9; K_2S, KSH, K_2S_3, K_2S_4, K_2S_5, K_4S_5, and K_4S_9.

P. 22, N. 2: Ammonium Salts of the Sulphoacids. — The following ammonium sulphosalts have all been prepared in the crystalline form by adding alcohol to concentrated solutions of the sulphides in ammonium sulphide: $(NH_4)_3AsS_3$ and $(NH_4)_3AsS_4$ (Berzelius, *Pogg. Ann.*, **7**, 141 and 18. 1826); $(NH_4)_3SbS_3$ (Pouget, *Ann. chim. phys.* (7), **18**, 532. 1899); $(NH_4)_3SbS_4$, $(NH_4)_3SbS_4.4H_2O$ (Stanek, *Z. anorg. Chem.*, **17**, 121. 1898); $(NH_4)_2SnS_3.3H_2O$ and $(NH_4)_3SnS_3.7H_2O$ (Stanek, *loc. cit.*, p. 213). Certain other arsenous salts, including NH_4AsS_2, have also been prepared in the solid state. On evaporating a solution of Sb_2S_3 in $(NH_4)_2S$ in a vacuum at a low temperature, the meta salt NH_4SbS_2 is usually obtained; on evaporating at a high temperature, or on treating NH_4SbS_2 with water, solid $(NH_4)_2Sb_4S_7$ is formed. Berzelius states that a solution of the empirical composition $(NH_4)_2S$ saturated with As_2S_3 or As_2S_5 contains these substances in the proportion $As_2S_3 : 2(NH_4)_2S$ or $As_2S_5 : 2(NH_4)_2S$. Pouget finds that a solution of $(NH_4)_2S$ saturated with Sb_2S_3 contains less antimony than corresponds to the ratio $Sb_2S_3 : 3(NH_4)_2S$. A K_2S or Na_2S solution dissolves sufficient Sb_2S_3 to give a solution of the composition $Sb_2S_3 : 2K_2S$ or $Sb_2S_3 : 2Na_2S$. There does not appear to be any direct evidence as to the nature of these salts in solution.

*Solid sulphosalts of the rare elements have been obtained from alkaline sulphide solutions as follows: K_3AuS_3 (Antony and Lucchesi, *Gazz. chim. ital.*, **26**, 359. 1896); $3K_2S.TeS_2$, $3Na_2S.TeS_2$, and $3(NH_4)_2S.TeS_2$ (Berzelius); K_2MoS_4, $(NH_4)_2MoS_4$ (Berzelius, *Pogg. Ann.*, **7**, 429. 1826; Krüss, *Liebig's Ann. Chem.*, **225**, 29. 1884).

P. 22, N. 4: Solubility of the Sulphides of the Tin and Copper Groups in Ammonium Hydroxide, Monosulphide, and Polysulphide. — 500 mgm. As as As_2S_3, Sb as Sb_2S_3, Sn as SnS, Cu as CuS, Hg as HgS, Cd as CdS, Bi as Bi_2S_3, all freshly precipitated by H_2S, and 500 mgm. As as As_2S_5, 100 or 500 mgm. Sb as Sb_2S_5, and 100 or 500 mgm. Sn as SnS_2 all precipitated from ammonium polysulphide, were warmed (but not enough to cause boiling through escape of gas) in a covered casserole for about 5 minutes with (*a*) 15–20 ccm. NH_4OH (0.96); (*b*) 10 ccm. of the ammonium monosulphide reagent; and (*c*) 10 ccm. of the ammonium polysulphide reagent. The solutions were then filtered and the filtrates acidified with HCl. The amount dissolved was estimated from the size and color of the precipitate or from the amount of the undissolved residue. The results are given below: the numbers represent roughly the number of milligrams of the element dissolved, a + sign indicating that this amount dissolved readily and that probably much more would have dissolved.

	(*a*) NH_4OH (0.96).	(*b*) Monosulphide.	(*c*) Polysulphide.
As_2S_3	500 +	500 +	500 +
As_2S_5	500 +	500 +	500 +
Sb_2S_3	0.5–1	50–100	500
Sb_2S_5	100[1]	300	500 +
SnS	0[2]	0–3[2]	500
SnS_2	100[1]	300	500 +
CuS	0–0.3	0	5–10
HgS	3–10	0	1
CdS	0	0	0
Bi_2S_3	0	0	0

[1] Only about 100 mgm. of the element as sulphide was taken in these experiments.

[2] A few milligrams (5–15) of a yellow precipitate (SnS_2), containing little or no SnS were precipitated on acidifying the filtrate.

The orange Sb_2S_3 was found to be changed into the black variety, stibnite, by continued treatment with ammonium monosulphide, and black HgS was changed into the red modification by continued treatment with the polysulphide. It was also noted that the HgS which dissolves in NH_4OH may be precipitated by adding a few drops of monosulphide.

500 mgm. Cu and 500 mgm. Hg as freshly precipitated sulphides were in separate experiments warmed to 50° or 60° in covered casseroles with 25 ccm. ammonium monosulphide for 15 minutes; the residues were filtered off, and the filtrates made acid with HCl: a slight precipitate of sulphur separated, which was only very slightly darkened, thus showing that only an insignificant quantity of CuS or HgS had dissolved.

An ammonium monosulphide solution was prepared from NH_4OH (0.90) as described in N. 2, except that the solution was not diluted with the equal volume of water. From this solution several different ammonium polysulphide solutions were prepared, containing, respectively, 20, 10, 5, 3, and 1 grams dissolved sulphur in 200 ccm., and their solvent power for SnS and CuS tested as follows:

500 mgm. Sn as freshly precipitated SnS were warmed gently in a covered casserole with (*a*) 10 ccm. of these undiluted solutions; (*b*) 5 ccm. of them + 5 ccm. water; and (*c*) 5 ccm. of them + 10 ccm. water. The mixture was stirred frequently with a glass rod. The amount of tin in milligrams dissolved in a solution containing x grams dissolved sulphur in 200 ccm. and the time required to dissolve it are given below.

	$x = 10$ g.	$x = 5$ g.	$x = 3$ g.	$x = 1$ g.
(*a*) 10 ccm. undiluted	500 4 minutes	500 5 minutes	500 15 minutes	100 5 minutes
(*b*) 5 ccm. + 5 ccm. H_2O . . .	500[1] 5 minutes	500 10 minutes	. .	100 10 minutes
(*c*) 5 ccm. + 10 ccm. H_2O . .	500 8–10 minutes	. .	. .	. .

500 mgm. Cu as CuS were similarly treated for 5 minutes: the following table shows roughly the number of milligrams Cu as CuS that dissolved in a solution containing x grams dissolved sulphur in 200 ccm. where x has the stated values.

	$x = 20$ g.	$x = 10$ g.	$x = 5$ g.	$x = 3$ g.	$x = 1$ g.	$x = 0$ g.
(*a*) 10 ccm. of solution	25 +	. .	12	6	0.5	. .
(*b*) 5 ccm. + 5 ccm. H_2O . . .	. .	8[1]	4	3	0.2	0
(*c*) 5 ccm. + 15 ccm. H_2O . . .	. .	6–8	. .	. .	. .	. .

[1] The regular reagent described in N. 2 has this composition.

*P. 22, *N. 5: Solubility of the Sulphides of the Rarer Elements in Ammonium Sulphide.* — Ribau (*Bull. soc. chim.*, **28**, 241. 1877) has shown that pure, freshly precipitated PtS_2 is nearly insoluble in ammonium sulphide, but dissolves in large quantity when mixed with sulphides of either the tin or copper groups. — Under "Test Analyses of the Tin Group" it is shown that small quantities of platinum and gold divide almost equally between the copper and tin groups when copper is also present.

50 mgm. Mo as freshly precipitated sulphide were digested in a covered casserole at 40–60° with 25 ccm. ammonium monosulphide for 15 minutes; the deep red solution was filtered and acidified with HCl: a precipitate estimated to contain about 35 mgm. Mo separated. The residue was digested a second time with 25 ccm. ammonium monosulphide: only about half the residue dissolved. — The experiment was repeated, using 10 ccm. portions of ammonium polysulphide: the result was the same, about two-thirds dissolving in the first treatment and about half the residue in the second.

200 mgm. Te were freshly precipitated with H_2S from a hot HCl solution containing 4 ccm. HCl (1.12) and 36 ccm. water; the black precipitate was digested with 25 ccm. ammonium monosulphide: the precipitate dissolved

completely in 3 or 4 minutes. The solution was acidified with HCl: a black precipitate separated. This was digested with 10 ccm. ammonium polysulphide; it dissolved immediately. To the solution HCl was added: a black precipitate separated.

200 mgm. Se as H_2SeO_3 were precipitated by Na_2SO_3 in an HCl (1.12) solution, as in *P. 43*c*. The red precipitate was filtered off and washed with HCl (1.12). It was then dissolved in hot HNO_3 (1.20); the solution was evaporated just to dryness and the residue dissolved in 4 ccm. of HCl (1.12) and 36 ccm. of water. The solution was heated to boiling and saturated with H_2S. A yellow precipitate which partly changed to red during the precipitation was produced. The solution was diluted to 100 ccm. and again saturated with H_2S in the cold; the precipitate was filtered off and digested with 25 ccm. ammonium monosulphide: the finely divided portion of the precipitate dissolved in a few minutes, forming a deep red solution, but the larger particles turned black on the surface and dissolved very slowly. After a few minutes the solution was filtered and the black residue digested successively three times with a fresh 25 ccm. portion of ammonium monosulphide: finally it all dissolved. The successive sulphide solutions were acidified with HCl (1.12): a bright yellow precipitate formed at first in every case, but that in the first solution gradually became orange within a few hours.

P. 22, N. 6: Extraction by Ammonium Monosulphide and Polysulphide of Arsenic, Antimony, and Tin Sulphides from those of the Copper Group. — See "Test Analyses of Tin Group."

Mixtures of 5, 10, 15, and 20 mgm. Sn as SnS with 500 mgm. Cd as CdS were digested at 80–90° with the ammonium polysulphide reagent in a pressure bottle for half an hour, and the solutions were analyzed by P. 41–47: the results recorded as in the Test Analyses were as follows:

Cd	500	500	500	500
Sn	5 F	10 F	15 D	20 S

The confirmatory test for tin (P. 47) failed in the experiment with 15 mgm. Sn. — The experiment was repeated with a mixture of 5 mgm. Sn as SnS_2 and 500 mgm. Cd as CdS: a small but satisfactory test for tin was obtained.

P. 22, N. 8: Coagulation of Colloidal Sulphides by NH_4NO_3. — In washing the various sulphides of the copper groups after the $(NH_4)_2S$ treatment, CuS, and especially CdS, sometimes passed through the filter in colloidal condition. To these colloidal mixtures was added enough solid NH_4NO_3 to make a 5% solution, and the mixtures were shaken and filtered: the filtrates were clear.

Analysis of the Copper Group

P. 23, N. 1: Solubility of the Copper Group Sulphides in HNO_3. — 500 mgm. of Pb, Bi, Cu, and Cd as sulphides were treated in separate experiments according to P. 23: the sulphides dissolved almost completely when the solution began to boil, but the sulphur residue remained dark-colored (except in the case of cadmium) even after several minutes' boiling.

500 mgm. Pb, Bi, Cu, and Cd as sulphides were in separate experiments boiled in an open casserole with about 30 ccm. of a mixture of one volume HNO_3 (1.20) and three volumes of water: Bi_2S_3 and CuS dissolved in 5 minutes or less, PbS dissolved less readily, and CdS only after 10–15 minutes. — The experiment was repeated, except that 50 ccm. of a still more dilute acid was used: the result was the same, except that solution took place somewhat less rapidly.

500 mgm. Hg as HgS were treated according to P. 23; and the filtrate was evaporated with excess of HCl to a small volume, diluted, and saturated with H_2S: a precipitate of HgS estimated to contain less than 1 mgm. Hg resulted. — The experiment was repeated, except that 30 ccm. HNO_3 (1.20) were used and the boiling continued for 10 minutes: a precipitate of HgS estimated to contain 2 mgm. Hg resulted. — The experiment was repeated, except that 30 ccm. of a mixture of one volume of HNO_3 (1.20) and three volumes of water were used and the boiling continued for 10 minutes: a precipitate of HgS containing about 0.5 mgm. Hg was formed. — 1 mgm. Hg as HgS was boiled with HNO_3 (1.20) for 10 minutes: no change in the amount of the sulphide was apparent.

P. 23, N. 4: Action of Strong HNO_3 on HgS. — 500 mgm. Hg as HgS were boiled for 10 minutes with 30 ccm. HNO_3 (1.42): the black precipitate had then become pure white. The filtrate was freed from HNO_3 and saturated with H_2S: a precipitate containing several milligrams Hg was formed. — The experiment was repeated, replacing the HNO_3 (1.42) by the strength used in P. 23: no change in the appearance of the precipitate took place.

P. *23, N. 5: Action of Dilute HNO_3 on Au and PtS_2.* — That small quantities of gold and platinum are not dissolved in P. 23 is shown by the results of Test Analyses, Nos. 106–113.

P. *23, N. 6: Oxidation of PbS to $PbSO_4$.* — 500 mgm. Pb as freshly precipitated PbS were treated according to P. 23, and to the filtrate $BaCl_2$ was added in large quantity: a precipitate of $BaSO_4$ estimated to correspond to 20–30 mgm. Pb was formed. — The experiment was repeated, except that the sulphide was boiled for 10 minutes with a more dilute acid, containing one volume HNO_3 (1.20) and three volumes water: the result was the same. — The experiment was repeated, except that HNO_3 (1.20) was used and the mixture boiled for 10 minutes: there was left with the sulphur

a small white residue of $PbSO_4$, estimated to contain 5 mgm. Pb, showing that the amount of H_2SO_4 formed increases with the HNO_3 concentration.

Solubility of $PbSO_4$ in Dilute HNO_3. — To 50 and 100 mgm. Pb as $PbSO_4$ in separate experiments 30 ccm. of a mixture of one volume HNO_3 (1.20) and three volumes of water were added and the mixtures heated: the 50 mgm. dissolved in the cold, the 100 mgm. upon boiling.

P. 23, N. 7: Action of HNO_3 on SnS, SnS_2, and Sb_2S_3. — 10 mgm. Sn as SnS and 10 mgm. Sn as SnS_2 were in separate experiments treated by P. 23: there was a white residue in each case. The filtrate was evaporated with H_2SO_4 to slight fuming, diluted, and saturated with H_2S: a yellow precipitate of SnS_2 estimated to contain 0.5 mgm. Sn was formed.

10 mgm. Sb as freshly precipitated Sb_2S_3 were treated by P. 23: the orange color of the sulphides disappeared at once, and a small white precipitate separated, which was estimated to contain 3–4 mgm. Sb. — The experiment was repeated with 5 mgm. Sb: no white residue was left. — The filtrates in these two experiments were made alkaline with NH_4OH: no precipitate of antimony hydroxide separated, even on standing.

P. 24, N. 1: Behavior of HgS, PtS_2, Au, and Metastannic Acid towards Bromine Solution. — 100 mgm. Hg and 500 mgm. Hg as precipitated HgS were warmed slightly in a covered casserole with 30–40 ccm. saturated Br_2 solution: the 100 mgm. dissolved completely, and about three-fourths of the 500 mgm. dissolved. The latter was treated with another portion of bromine water: the residue became nearly white, but blackened slightly when treated with ammonium sulphide.

The experiment was repeated with 10 mgm. Sn as metastannic acid, obtained by treating SnS with dilute HNO_3 by P. 23, the solution was boiled, filtered, and saturated with H_2S: scarcely any precipitate of SnS_2 was formed. — That even small quantities of Au and PtS_2 dissolve in bromine solution is shown by the results of Test Analyses, Nos. 106–113.

P. 24, N. 2: Reduction of Hg_2Cl_2 by $SnCl_2$. — To 1 mgm. Hg as $HgCl_2$ in 20 ccm. water one drop $SnCl_2$ solution (1 % Sn) was added: a nearly white precipitate formed at once. One or two drops more $SnCl_2$ were added: the precipitate darkened rapidly. — The experiment was repeated, except that 0.3 to 0.5 ccm. HCl (1.12) was added to the $HgCl_2$ solution before the $SnCl_2$: a precipitate formed, which remained white for some minutes, even after the addition of several drops of $SnCl_2$ solution.

P. 24, N. 3: Oxidation of Mercurous Salts by HNO_3. — See Part I, C. E., P. 3, N. 7.

P. 24, N. 4: Color of Dilute Solutions of Gold and Platinum. — 1 mgm. Au as $AuCl_3$ and 1 mgm. Pt as H_2PtCl_6 were added in separate experiments to 20 ccm. water and boiled: the solutions had a very pale yellow color, but this color was distinct. A few drops of bromine water were added, and

the solutions were boiled to expel the bromine: the yellow color was more distinct than before.

**P. 24a, N. 1: Detection of Gold, Platinum, and Mercury in the Presence of Each Other.* — Mixtures of elements as shown below dissolved in a little dilute HCl were treated by *P. 24*a*; and the tests, recorded as in the Test Analyses, resulted as follows:

Pt	0 —	0 —	1 S	50 S
Au	10 S	1 S	1 S	0 —
Hg	1 S	200 S	200 —	1 S

P. 25, N. 1: Separation of Metastannic Acid from HgS. — See Test Analyses, Nos. 10–20.

P. 26, N. 1: Solubility of $PbSO_4$ in Water and H_2SO_4. — According to Böttger (*Z. phys. Chem.*, **46**, 604. 1903), 10 ccm. of the saturated solution in water at 25° contain about 0.3 mgm. Pb. — For its solubility in concentrated H_2SO_4 of different strengths, see Comey, *Dictionary of Solubilities*, p. 436.

To determine at what concentration of H_2SO_4 the precipitation was nearly complete, several 2 mgm. portions of Pb as $Pb(NO_3)_2$ were evaporated to fuming with 5 ccm. H_2SO_4 (1.84), and the clear solutions obtained were poured into varying amounts of water; the mixtures were cooled, shaken, allowed to stand for a few minutes, filtered, made alkaline with NH_4OH, and treated with H_2S: with 10, 15, and 20 ccm. water, the final alkaline solution remained almost colorless when treated with H_2S, thus showing that the amount of lead remaining in the filtrate was scarcely appreciable; when as much water as 50 ccm. was used, the liquid was much darkened by H_2S and a small precipitate of PbS separated on standing.

Influence of HNO_3 on the Solubility of $PbSO_4$. — See C. E., P. 23, N. 6.

To each of several solutions containing 1 mgm. Pb as $Pb(NO_3)_2$ in 5 ccm. HNO_3 (1.20) and 15 ccm. water were added 2 ccm. of H_2SO_4 (1.84); the mixture was shaken violently and allowed to stand: only in one or two cases did a precipitate of $PbSO_4$ separate within 10 minutes. 3 ccm. more H_2SO_4 were then added to the solutions that remained clear: $PbSO_4$ precipitated in every case. — The experiment was repeated, except that 2 mgm. Pb were taken: a precipitate of $PbSO_4$ separated when the 2 ccm. H_2SO_4 were added. — To 1 or 2 mgm. Pb in 10 ccm. HNO_3 (1.20) and 10 ccm. water 2 ccm. H_2SO_4 were added: no precipitate resulted. 3 ccm. H_2SO_4 more were added: when 2 mgm. Pb were present, a precipitate formed. — The last experiment was repeated with 4 mgm. Pb, using 2 ccm. H_2SO_4 (1.84): a precipitate of $PbSO_4$ separated.

P. 26, N. 2: Separation of Bismuth from H_2SO_4 Solutions. — 500 mgm. Bi as nitrate were evaporated to fuming with 5 ccm. H_2SO_4 (1.84) and cooled: a large quantity of a white solid separated. The mixture was added to 20 ccm. cold water and cooled: almost all dissolved, only a very small white residue (2–3 mgm.) being left, which was proved by P. 14 not to be $PbSO_4$; but on standing overnight a large, coarsely crystalline white precipitate (probably bismuth oxysulphate) separated. This was filtered off and the filtrate made alkaline with NH_4OH: a precipitate estimated to contain 40–80 mgm. Bi separated. In another experiment the filtrate, instead of being treated with NH_4OH, was diluted with two volumes of water and allowed to stand: more of the precipitate separated slowly. — The experiment was repeated, except that the clear solution obtained on dilution with cold water was heated to boiling: a large white precipitate separated at once, which was similar in appearance to that obtained in the former experiment; this did not dissolve when the solution was cooled and shaken. — Separate portions of the white precipitates which had separated in the preceding experiments from the dilute H_2SO_4 solution on standing, and on heating, were treated with 30–40 ccm. cold H_2SO_4 (1.20): the precipitates dissolved only slightly, even on standing. The undissolved precipitates still containing about 300 mgm. Bi were collected on filters and about 10 ccm. HCl (1.12) poured over each: clear solutions were quickly obtained.

P. 27, N. 1: Nonprecipitation of Small Quantities of Antimony by NH_4OH. — Compare C. E., P. 23, N. 7.

10 mgm. Sb as $SbCl_3$ and 2 ccm. H_2SO_4 (1.84) were added to 10 ccm. water; the mixture was evaporated to fuming, cooled, diluted to 15 ccm., made just alkaline with NH_4OH, and allowed to stand for 30 minutes: no precipitate separated; but when 10 ccm. more NH_4OH (0.96) were added, a very slight white precipitate separated. — The experiment was repeated, except that the $SbCl_3$ solution was first warmed with HCl + HNO_3 to convert it into the antimonic state: no precipitate separated from the NH_4OH solution, even on standing.

P. 27, N. 2: Complex Copper-Ammonia and Cadmium-Ammonia Cathions. — See Dawson and McCrae, *J. Chem. Soc.*, **77**, 1239 (1900); Euler, *Ber. d. chem. Ges.*, **36**, 3400 (1903); Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904); Locke and Forssell, *Am. Chem. J.*, **31**, 268. (1904).

P. 28, N. 1: Precipitation of BiOCl. — To 0.25 ccm. HCl (1.20) was added 1 mgm. Bi as chloride, and the solution poured into 100 ccm. water at 60°: a precipitate of BiOCl appeared in about a minute. After 5 minutes the solution was filtered, made alkaline with NH_4OH, and treated with H_2S: no precipitate formed. — The experiment was repeated, using 0.5 ccm. HCl (1.20) instead of 0.25 ccm.: no precipitate of BiOCl formed in 5 minutes. — It was again repeated, using 0.5 ccm. HCl and 2 mgm. Bi: a

precipitate of Bi had formed after 5 minutes, but the filtrate also gave a precipitate with H_2S. — It was again repeated, using 1 ccm. HCl (1.20) and 6 and 8 mgm. Bi: with 8 mgm. Bi a precipitate formed, but not with 6 mgm.

In a number of experiments 1 mgm. Bi dissolved in 0.25 ccm. HCl (1.20) was poured into 100 ccm. water at various temperatures: a precipitate of BiOCl appeared in less than 1 minute when the temperature was 55°, 70°, 80°, or 90°, in about 2 minutes at 45°, in about 5 minutes at 25°, and only after 10–15 minutes at 15°.

P. 28, N. 2: Decomposition of Sodium Stannite Solution. — A sodium stannite solution was prepared as directed and kept in a stoppered bottle for a week: a black, crystalline deposit appeared at the bottom of the bottle.

P. 28, N. 3: Action of Sodium Stannite on BiOCl. — Vanino and Treubert (*Ber. d. chem. Ges.*, **31**, 1113. 1898) have shown that the black precipitate formed by the action of a stannite solution is metallic bismuth, and not BiO, as was formerly supposed to be the case.

0.5 mgm. Bi as $BiCl_3$ was added in one experiment to 100 ccm. water, and in a second one to 500 ccm. water; the precipitate formed (which was scarcely visible in the second case) was collected on a filter, washed with water, and then treated with Na_2SnO_2: the greater part of the filter was at once blackened.

10 mgm. Pb as $Pb(OH)_2$ were treated on a filter first with a cold Na_2SnO_2 solution and then with a solution at about 60°: in the first case no blackening occurred in several minutes, while in the second it occurred almost immediately.

The experiment was repeated with 20 mgm. Sb as antimonous and with 20 mgm. Sb as antimonic hydroxide: no blackening was observed in either case.

The experiment with cold Na_2SnO_2 was repeated with 2 mgm. Fe as $Fe(OH)_3$: the red precipitate did not change color in 10 minutes; but, when hot Na_2SnO_2 was poured over it, it slowly became darker.

P. 29, N. 1: Precipitation of Copper Ferrocyanide in the Presence of a Cadmium Salt. — A solution containing 1 mgm. Cu as $CuSO_4$, 500 mgm. Cd as $Cd(NO_3)_2$, and 2 ccm. H_2SO_4 (1.84) was made alkaline with NH_4OH: the solution remained colorless. One-fourth of the solution (about 10 ccm.) was acidified with acetic acid and two drops of a 4% $K_4Fe(CN)_6$ solution added: a white precipitate separated, which had at first only a slight pink tinge, but this color deepened and was very apparent after 10 minutes. Excess of $K_4Fe(CN)_6$ was then added: much more of the white precipitate separated, and the pink color of the copper salt was almost obscured. — The experiment was repeated, except that only 0.5 mgm. Cu was taken: the result was exactly the same, thus showing that this test is a very deli-

cate one, provided only two to three drops of $K_4Fe(CN)_6$ solution are first added.

P. 29, N. 2: Precipitation of Molybdenum by Potassium Ferrocyanide. — 1 and 100 mgm. Mo as MoO_3, and 1 and 10 mgm. U as $UO_2(C_2H_3O_2)_2$, in separate experiments were dissolved in 2 ccm. NH_4OH (0.96), the solutions made acid with acetic acid, and several drops of $K_4Fe(CN)_6$ solution added: no change was observed. — The experiments were repeated, except that the NH_4OH solution was acidified with HCl instead of with acetic acid: with the 100 mgm. Mo and the 10 mgm. U a large dark red precipitate separated at once: with the 1 mgm. portions a deep red solution was obtained, from which a dark red precipitate separated after a minute or two.

P. 30, N. 1 and 2: Complex Cuprocyanide and Cadmicyanide Anions. — See Euler, *Ber. d. chem. Ges.*, **36**, 3404 (1903); Bodländer, *Ber. d. chem. Ges.*, **36**, 3933 (1903).

P. 30, N. 3: Behavior of Mercury, Lead, and Bismuth in the Cadmium Test with H_2S. — 1 mgm. Hg, 1 mgm. Pb, and 1 mgm. Bi were treated in separate experiments by P. 26, 27, and 30, filtering immediately after the addition of H_2SO_4 and of NH_4OH: there resulted a precipitate with H_2SO_4 in the case of lead and with NH_4OH in the case of bismuth, but none in the case of mercury with these reagents. With H_2S in the KCN solution small dark brown precipitates formed in the lead solution and in the mercury solution, and a very small black one in the bismuth solution. — The experiment was repeated with 150 mgm. Pb and with 150 mgm. Bi, the precipitates of $PbSO_4$ and of $(BiO)_2SO_4$ and $Bi(OH)_3$ being filtered after cooling and standing a few minutes: even less precipitate resulted in each case than when only 1 mgm. was used.

Separation of CdS from Black Sulphides by Dilute H_2SO_4. — 1 mgm. Cd as CdS, freshly precipitated by H_2S from an NH_4OH solution, was boiled gently for about 5 minutes with 20 ccm. of a mixture of one volume of H_2SO_4 (1.20) with four volumes of water; the solution was filtered, diluted with two to three times its volume of water, and saturated with H_2S in the cold: a yellow precipitate of CdS separated.

The experiment was repeated, except that in separate experiments 1 mgm. Cu, 1 mgm. Pb, and 1 mgm. Hg were mixed with 1 mgm. Cd: a distinctly yellow precipitate was obtained in each experiment.

About 50 mgm. Cd as CdS were boiled for 5 minutes with 20 ccm. of a mixture of one volume H_2SO_4 (1.20) and four volumes of water: the sulphide did not dissolve completely.

Analysis of the Tin Group

P. 41, N. 1: Detection of the Tin Group by the Appearance of the HCl Precipitate from the Ammonium Polysulphide Solution. — Separate 10 ccm.

portions of the ammonium polysulphide reagent (see P. 41, N. 2) were diluted to known volumes in some experiments with hot water, and in others with cold water; the solutions were then made acid by adding HCl slowly, and the mixtures were shaken and allowed to stand: from cold solutions of a total volume of 30 to 50 ccm. the sulphur separated as a pure white, finely divided precipitate, which coagulated slowly on shaking, and had then only a faint yellow tinge which did not change on warming. From more concentrated solutions, and especially from hot solutions, the yellow color after coagulation was more pronounced. Separate 10 ccm. portions of the ammonium polysulphide reagent containing 1 mgm. As were diluted with 20 ccm. and with 40 ccm. water; HCl was slowly added until the solutions were acid; the mixtures were shaken and allowed to stand: the precipitate had at first the appearance of pure sulphur, but it coagulated more quickly, became flocculent, and turned brilliant yellow. Further experiments showed that the coagulation and change of color took place more quickly when the mixture was slightly warmed after coagulation. — The experiment was repeated, using 1 mgm. Sb instead of As: the HCl precipitate remained white as long as the solution remained alkaline, but on further addition of HCl the orange color of the Sb_2S_5 became very apparent; the precipitate quickly coagulated and became flocculent. — The experiment was repeated with 1 mgm. Sn: the HCl precipitate had a very faint yellow tinge; it coagulated only slowly, and appeared like the pure sulphur precipitate, except that it had a much darker yellow color. The experiment was repeated with 1 mgm. Cu as $CuSO_4$: a dark orange-yellow (liver-colored) precipitate was obtained. — The experiment was repeated with 1 mgm. Hg as $HgCl_2$: the HCl precipitate was nearly white, but when warmed slightly it became dark gray in color.

Color of a Mixture of Tin and Antimony Sulphides. — 500 mgm. Sn as $SnCl_2$ and 200 mgm. Sb as $SbCl_3$ were slowly added to 10 ccm. of a warm ammonium polysulphide solution, and the clear solution obtained was at once acidified with HCl: a brown precipitate separated, which slowly became dark gray in color. — The experiment was repeated, except that the ammonium polysulphide solution was cooled and diluted to about 40 ccm. and HCl was slowly added: the precipitate was at first yellow with an orange tint, but on standing it slowly became darker, assuming first a brown and finally a dark gray color. — These precipitates were treated by P. 42–47: the antimony and tin dissolved completely in HCl (1.20) (P. 42), and the antimony was completely precipitated in P. 45 as an orange precipitate.

P. 41, N. 2: Solubility of Tin-Group Sulphides in NH_4OH. — See C. E., P. 22, N. 1.

For evidence that salts of intermediate sulpho-oxyacids of arsenic are formed when As_2S_5 is dissolved in an alkali, see McCay, *Ber. d. chem. Ges.*,

32, 2471 (1899); *Z. anorg. Chem.*, **25**, 459 (1901); McLouchlan, *Ber. d. chem. Ges.*, **34**, 2166 (1901); Weinland and Lehman, *Z. anorg. Chem.*, **26**, 322 (1901). Treadwell (*Qual. Anal.*, p. 188. 1902) concludes that K_3SbO_3 is not formed by the action of KOH on Sb_2S_3 according to the equation $Sb_2S_3 + 6KOH = K_3SbO_3 + K_3SbS_3 + 3H_2O$, because this solution is stable when diluted, while a solution of K_3SbO_3 is not.

For evidence that the precipitation of arsenic is incomplete when a solution of As_2S_5 in an alkali is made acid, see Weinland and Lehman, *loc. cit.*, and Vanino and Griebel, *Z. anal. Chem.*, **40**, 589 (1901).

Presence of Copper and Mercury in the Tin Group. — For the solubility of CuS and HgS in NH_4OH and in ammonium mono and polysulphide, see C. E., P. 22, N. 4. — For the fact that copper and mercury will divide in the heating with HCl (1.20), see C. E., P. 42, N. 6. — That the presence of even 2 mgm. Cu or of Hg does not interfere with the detection of arsenic is shown in C. E., P. 43, N. 3. — That the same amount of copper or mercury does not prevent the detection of antimony is shown in C. E., P. 46, N. 1.

P. 42, N. 1: Solubility of Sb_2S_5 in HCl (1.20). — 500 mgm. Sb as sulphide, freshly precipitated from an ammonium polysulphide solution, and therefore consisting mainly of Sb_2S_5, were treated according to the procedure: nearly all the antimony dissolved, but the sulphur residue had an orange-red color. The residue was treated a second time in the same way, and the HCl solution diluted and saturated with H_2S: a small precipitate of Sb_2S_3 estimated to contain 1 or 2 mgm. Sb formed. The sulphur residue was again treated with HCl: scarcely any Sb dissolved, although the residue still had a distinct orange color.

A mixture of 1 mgm. Sb as Sb_2S_5 with 500 mgm. As as As_2S_5 (freshly precipitated from an ammonium polysulphide solution and carefully dried by suction) was treated by the procedure, and the residue subjected to a second and then to a third treatment; the separate HCl solutions were diluted and treated with H_2S by P. 45: the first solution contained about 0.6 mgm. Sb, the second about half this amount, and the third only a trace. — This experiment was repeated, except that the sulphides were not carefully dried before adding HCl (1.20): the second HCl solution contained more Sb than the first, thus showing that the presence of water interferes with the action of the HCl.

Formation of $SbCl_3$ by Dissolving Sb_2S_5 in HCl. — See Classen and Bauer, *Ber. d. chem. Ges.*, **16**, 1067 (1883).

P. 42, N. 2: Solubility of As_2S_5 in HCl (1.20). — Seven different 500 mgm. portions of As as As_2S_5, freshly precipitated from an ammonium polysulphide solution, were treated by the procedure; and the filtrates were warmed and saturated completely with H_2S: only a faint precipitate resulted, in no case corresponding to more than a small fraction of a milligram of

arsenic. — The experiment was repeated, except that the HCl (1.20) was boiled gently for 5 minutes: the filtrate was found to contain 5–10 mgm. As. The vapors given off blackened lead acetate paper held above the flask.

P 42, N. 3: Solubility of As_2S_3 in HCl (1.20). — Six separate 500 mgm. portions of As as As_2S_3, freshly precipitated from H_3AsO_3 solution by H_2S in five of the experiments and by acidifying a solution of As_2S_3 in NH_4OH in the remaining one, were treated by the procedure and the filtrate saturated with H_2S: in each experiment distinct precipitates of As_2S_3 were obtained, which were estimated to contain between 1 and 5 mgm. As. — The experiments were repeated, except that a slow current of H_2S was passed through the HCl during the experiment: the filtrates then gave with H_2S scarcely any precipitate — A solution of 100 mgm. As as As_2O_3 in 20 ccm. HCl (1.20) was saturated with H_2S for 5 minutes at about 90°, the solution decanted off, water added, and H_2S again passed in: no more precipitate separated.

P. 42, N. 6: Solubility of CuS and HgS in HCl. — 10 mgm. Cu as CuS and 10 mgm. Hg as HgS, freshly precipitated, were treated in separate experiments by P. 42: the greater part but not all of each of the precipitates was dissolved.

**Solubility of TeS_2 in HCl (1.20).* — 50 mgm. Te as TeO_2 dissolved in HCl were added to 10 ccm. ammonium polysulphide; the solution was treated by P. 41, the black HCl precipitate was heated with HCl (1.20) by P. 42, and the filtrate was saturated with H_2S: a precipitate formed estimated to contain about 1 to 2 mgm. Te. — The experiment was repeated, except that the HCl solution was kept saturated with H_2S: in this case no tellurium dissolved.

**Insolubility of Sulphides of Pt, Au, Se, and Mo in HCl (1.20).* — 20 mgm. Pt, 10 mgm. Au, 50 mgm. Se, and 50 mgm. Mo, all as sulphides precipitated by acidifying an ammonium polysulphide solution, were in separate experiments digested at about 90° for 10 minutes with 10 ccm. HCl (1.20), diluted, and filtered, as described in P. 42; the filtrates were saturated with H_2S at 100°, diluted to 50 ccm., again heated and saturated with H_2S: no precipitate separated in any case, not even after several minutes, thus showing that nothing had dissolved in the HCl.

P. 43, N. 1: Reactions between $HClO_3$ and HCl. — See Schacherl, *Liebig's Ann. Chem.*, **182**, 193 (1876); Bray, *Z. anorg. Chem.*, **48**, 242 (1906).

P. 43, N. 2: Nonexistence of $AsCl_5$. — See Smith and Hora, *J. Am. Chem. Soc.*, **26**, 632 (1904). For earlier references, see Baskerville and Bennet, *J. Am. Chem. Soc.*, **24**, 1070 (1902).

Non-volatility of Arsenic Acid from HCl Solution. — 2.0 grams As as As_2O_5, containing a small amount of As_2O_3, were dissolved in 20 ccm. HCl (1.20)

and distilled until only half the volume remained in the flask; 10 ccm. more of HCl (1.20) were added and the solution distilled as before; and this operation was repeated several times; the distillates were collected in separate portions of cold water and saturated with H_2S: in the first distillates yellow precipitates appeared at once, which decreased in amount from about 15 mgm. As in the first distillate to about 0.5 mgm. As in the fifth. (This was evidently due to the As_2O_3 present as impurity.) These solutions were filtered and the filtrates treated at 90° with H_2S for several minutes: very little, if any, precipitate was obtained, showing that arsenic in the higher state of oxidation was practically absent. From later distillates precipitates containing about 0.5 mgm. As separated quickly with H_2S in the cold, and no further precipitate separated when the solutions were heated and treated with H_2S. Thus even from this concentrated solution of arsenic acid in the presence of concentrated HCl only a trifling amount of arsenic volatilized. Since the higher halogen compound of an element is in general more volatile than the lower, it is therefore highly probable, from the above result, that $AsCl_5$ is not present even in concentrated HCl solution.

P. 43, N. 3: Non-influence of Mercury, Antimony, or Tin on the Test for Arsenic with $MgCl_2$. — 2 mgm. Hg as $HgCl_2$, 2 mgm. Sn as $SnCl_4$, 2 mgm. Sb as Sb_2S_3 were treated in separate experiments according to the procedure: with mercury a precipitate was obtained with NH_4OH, and the filtrate when acidified with HCl and treated with H_2S gave no precipitate; with tin and antimony no permanent precipitate formed in the NH_4OH solution, nor was one formed with $MgCl_2$ and NH_4Cl.

P. 43, N. 4: Delicacy of Test for Arsenic. — 0.5, 1, and 2 mgm. As as H_3AsO_4 were treated in separate experiments according to P. 43, the final volume being in each case about 5 ccm.: with 2 mgm. the $MgNH_4AsO_4$ precipitate appeared immediately upon shaking; with 1 mgm., after gentle stirring; and with 0.5 mgm., slowly after rubbing with a glass rod for a minute or two.

**P. 43a, N. 2: Action of KI on K_2PtCl_6.* — To 5 mgm. Pt as H_2PtCl_6 were added 10 ccm. water and a few drops KI solution: a deep red solution resulted. 5 ccm. CS_2 were added and the mixture shaken: the water layer remained dark red, and the CS_2 solution was colored slightly, owing to the presence of a trace of iodine. The water layer was shaken with a fresh portion of CS_2: this time the CS_2 layer was colorless, thus proving that only an insignificant quantity of iodine was present, and therefore that the platinic compound is not reduced. To the solution some H_2SO_3 solution was added: the color of the solution changed at once to a pale yellow.

**P. 43b, N. 1: Action of Oxalic Acid on Solutions of Chlorauric, Selenous, Tellurous, and Molybdic Acids.* — 2 mgm. Au as $AuCl_3$ were dissolved in one experiment in a dilute HCl solution containing about 0.5 gram $H_2C_2O_4$, in

a second one in a dilute solution of NH_4OH and $(NH_4)_2C_2O_4$, and the solutions were evaporated to 3–4 ccm.: no precipitate separated in either case. The solutions were then evaporated almost to dryness to expel the excess of HCl and of NH_4OH, were diluted to about 15 ccm., and again boiled: a purple precipitate of gold quickly appeared in both cases. — In another experiment 0.5 mgm. Au as $AuCl_3$ was added to 10 ccm. of a dilute $(NH_4)_2C_2O_4$ solution which had been made slightly acid with $H_2C_2O_4$, and the solution was heated to boiling: a purple precipitate of gold separated.

5 mgm. Au as $AuCl_3$ were treated according to the procedure: a precipitate of gold appeared quickly and continued to separate for 2 or 3 minutes. After about 5 minutes the gold was filtered off and the filtrate again digested for several minutes on the steam bath: no further precipitate of gold separated.

50 mgm. Se as H_2SeO_3, 50 mgm. Te as H_2TeO_3, and 50 mgm. Mo as $(NH_4)_2MoO_4$ were treated in separate experiments by *P. 43*b*: in the case of tellurium a white precipitate separated from the $H_2C_2O_4$ solution on evaporation, but it dissolved readily on adding HCl; in the other two experiments no precipitate formed and no color change was noticed.

**P. 43c, N. 1: Action of H_2SO_3 on H_2SeO_3.* — 1 mgm. Se as SeO_2 in 10 ccm. HCl (1.15) was saturated with SO_2 gas at room temperature: a red precipitate appeared at once and continued to increase slowly. After 5 minutes the solution was filtered and the filtrate allowed to stand: it remained clear. — The experiment was repeated, except that the solution was saturated at 90°: a reddish precipitate appeared at once, but it changed rapidly to a very compact, nearly black precipitate that collected at the bottom of the test tube. — The first experiment was repeated with 0.5 mgm. Se: a considerable red precipitate separated within 5 minutes.

**P. 43c, N. 2: Action of H_2SO_3 on H_2TeO_3.* — 100 mgm. Te as TeO_2 were dissolved in separate experiments in 10 ccm. HCl (1.20), in 10 ccm. HCl (1.20) and 5 ccm. water, and in 20 ccm. HCl (1.12). Each solution in a test tube was saturated with SO_2 gas, was allowed to stand 5 minutes, and then placed in a steam bath at 100° for 15 minutes: no precipitate of tellurium was formed in any case. Enough water was added to make the volume 30 to 40 ccm.: a black precipitate of tellurium appeared at once.

In each of eight test tubes were placed 0.5 mgm. Te as TeO_2 and 25 ccm. saturated H_2SO_3 solution. To the first of these were added 3 ccm. 40% HCl, to the second 4 ccm., to the third 5 ccm., and so on up to the eighth, which contained 10 ccm.; the tubes were then all heated in a steam bath: those with 3 and 4 ccm. HCl gave scarcely any precipitate; in the others the quantity of precipitate increased with the increase of acid up to 7 ccm., and then decreased steadily with further increase in the amount of HCl.

**P. 43d, N. 1: Action of KI and of KI + H_2SO_3 on Tellurium*

Solutions. — For the formation of TeI_4 in the reaction between H_2TeO_3 and KI, see Gooch and Morgan, *Am. J. Sci.* (4), **2**, 271 (1896). For the formation of K_2TeI_6, see Wheeler, *Am. J. Sci.* (3), **45**, 267 (1893). For its deep red color, see Norris and Fay, *Am. Chem. J.*, **23**, 109 (1900).

To prove that tellurium itself and not an iodide of it is precipitated by H_2SO_3 and HI, 20 mgm. Te as TeO_2 were dissolved in 10 ccm. HCl (1.12) and 1 mgm. I as KI and a little solid Na_2SO_3 were added: a large black precipitate formed slowly. This was filtered off after half an hour, the filtrate was diluted to 20 ccm., and to it were added a few drops KI solution and a little solid Na_2SO_3: a black precipitate estimated to contain only 1 to 2 mgm. Te resulted. — The experiment was repeated, except that the mixture was allowed to stand overnight before filtering: only about 0.2 mgm. Te remained in solution.

To determine the proper concentration of HCl for the complete precipitation of the tellurium, a few drops of KI solution were added to solutions containing 0.5 mgm. Te as TeO_2 dissolved in 10 ccm. HCl (1.20), in 15 ccm. HCl (1.15), in 20 ccm. HCl (1.12), and in 30 ccm. HCl (1.06), respectively: a deep red color resulted in each case, but was less intense in the most concentrated and in the most dilute HCl than in the other two solutions. A crystal of Na_2SO_3 was added to each solution: no change was observed in the three more concentrated HCl solutions, but a black precipitate of tellurium formed in the most dilute solution. — In another experiment 0.1 mgm. Te was dissolved in 20 ccm. HCl (1.06), and a drop of KI and a crystal of Na_2SO_3 added: a black precipitate resulted.

50 mgm. Te as TeO_2 were treated according to the procedure, and the precipitated tellurium filtered off after 5 minutes: the filtrate had a strong odor of SO_2, but no more tellurium separated in half an hour, even when a little KI was added.

P. 43d, N. 2: Action of HI on H_2SeO_3.* — See Norris and Fay, *Am. Chem. J.*, **23, 109 (1900).

**P. 43d, N. 3: Action of HI on H_2MoO_4.* — To separate solutions of 50 mgm. Mo as MoO_3 in 10 ccm. HCl (1.20) and in 20 ccm. HCl (1.12) a few drops of KI solution were added: iodine was slowly liberated in both cases, but more rapidly in the more strongly acid solution.

**P. 43e, N. 2: Action of Zinc and KCNS on H_2MoO_4.* — To 1 mgm. Mo as MoO_3 dissolved in 20 ccm. HCl (1.06) in a test tube were added a crystal of KCNS and some granules of zinc: a brilliant red color appeared very quickly and remained unchanged for about 5 minutes; the color slowly changed to yellow, and then faded until after about half an hour the solution was nearly colorless. — The experiment was repeated, except that the KCNS was not added until after the action of the zinc had continued for 15 minutes: a yellow color resulted. — The experiment was repeated, except

that the KCNS was added after about an hour: the solution remained colorless.

For the composition of the red compound produced with KSCN and zinc, see Sand and Burger, *Ber. d. chem. Ges.*, **38**, 3384 (1905); **39**, 1761 (1906).

P. 44, N. 1 and 2: Action of H_2S on H_3AsO_4 Solutions. — See McCay, *Am. Chem. J.*, **10**, 459 (1888). Brauner and Tomicek, *J. Chem. Soc.*, **53**, 145 (1888). Usher and Travers, *J. Chem. Soc.*, **87**, 1370 (1905).

P. 45, N. 1: Separation of Antimony and Tin by H_2S. — Known amounts of Sb and Sn as chlorides were added to an ammonium polysulphide solution and precipitated as Sb_2S_5 and SnS_2 with HCl; the precipitates were dried by suction and digested with 10 ccm. HCl (1.20) at 90° for 10 minutes in a 50 ccm. conical flask. Each solution so obtained was diluted to a known volume and treated with H_2S just below the boiling point. The volume of the diluted solution at which the precipitation of Sb_2S_3 was nearly or quite complete and that at which the precipitation of SnS_2 began and became considerable are given in the following table:

Experiment No.	Sn	Sb	Volume of solution at which precipitation of antimony was		Volume of solution at which precipitation of tin	
			nearly complete.	complete.	began.	was considerable.
	mgm.	mgm.				
1	500	0	. .	. .	50	60
2	500	0	. .	. .	60	70
3	400	1	40	50	60	70
4	500	1	. .	50	60	70
5	500	1	. .	55	60	70
6, 7	500	200	40	50	60	70
8	10	500	40	50	. .	. .
9	200	200	. .	50	. .	. .
10	0	1	. .	55	. .	. .

In Experiment No. 1 a slight yellow precipitate of SnS_2 appeared in testing for antimony, but a good blank was obtained in No. 2. In Experiment 4 an orange-red precipitate of Sb_2S_3 was obtained; in Experiment 5 a dark-colored precipitate, which gave a good confirmatory test for antimony. In Experiment 10 the Sb_2S_3 precipitate did not separate until the last 5 ccm. of water were added.

P. 45, N. 2: Precipitation of CuS and HgS from HCl Solution. — 1 mgm. Cu and 0.5 mgm. and 4–5 mgm. Hg as chlorides were added in separate experiments to 10 ccm. HCl (1.20) and 40 ccm. H_2O, and the solutions were

heated to boiling and saturated with H_2S at 90°: in the first two cases light gray precipitates formed slowly, which on the filter appeared to be black; in the last case a black precipitate. The precipitates were filtered out, the solutions diluted and treated with H_2S: in the mercury experiments they gave no precipitates, but in the case of Cu a very slight precipitate formed.

P. 46, N. 1: Influence of Copper and Mercury on the Reduction Test for Antimony. — 1 and 2 mgm. Hg as HgS and 1 and 2 mgm. Cu as CuS were treated in separate experiments according to P. 46: the mercury separated on the platinum as a gray, loosely adhering film, the copper as a red, metallic, firmly adhering deposit, which could not be mistaken for antimony.

The experiments were repeated in the presence of 0.5 and 1 mgm. Sb: characteristic black deposits of Sb were obtained.

P. 46, N. 2: Behavior of Arsenic and Tellurium in the Reduction Test for Antimony. — 1, 4, and 10 mgm. As as H_3AsO_4 and 0.5 mgm. Te as H_2TeO_3 were treated in separate experiments according to P. 46: with the 10 mgm. As and with the tellurium black deposits on the platinum were obtained, which dissolved readily in a normal, cold alkaline solution of NaOCl; no deposit of arsenic was obtained with the 1 or 4 mgm. As. It is therefore improbable that a black deposit of arsenic will ever be obtained in an actual analysis, since only very small amounts will be dissolved in the HCl treatment (P. 42).

Insolubility of Sb in NaOCl. — 1 mgm. Sb precipitated on platinum foil by the action of HCl and Sn was treated in the cold for 5–10 minutes with a normal, alkaline NaOCl solution: no change took place.

P. 47, N. 1: Effect of Temperature on the Precipitation of SnS_2. — A solution of 1 mgm. Sn as $SnCl_4$ in 10 ccm. HCl (1.20) was successively diluted with portions of water and saturated with H_2S at 90° after each dilution: a precipitate formed only when the volume of the solution had become 110–120 ccm. — The experiment was repeated several times, except that the solutions were saturated for 5–10 minutes with H_2S at 20°: a precipitate formed when the volume became 60–70 ccm.

P. 47, N. 2: Delicacy of Confirmatory Test for Tin. — 0.5 Sn as $SnCl_4$ was treated in several experiments according to P. 47: in all cases a precipitate of SnS_2, and in most cases one of Hg_2Cl_2, was obtained.

THE PRICE OF ELECTRICITY[1]

By ROBERT SEVER HALE

I FEEL a little diffidence in addressing engineers on the subject of prices as distinct from the subject of costs. A reduction in costs, even if it does not lead to a reduction of prices, is always of benefit to somebody, and is of interest to engineers since it is always in the end for the general good. On the other hand, the question of prices may be and often is merely a commercial question between buyer and seller; nevertheless there are cases in which a scientific system of prices enables a lower price to be made to the purchaser without reducing the seller's gain, and the study of such a system comes easily within the well-known definition of an engineer as a man who can do for one dollar what any fool can do for two.

The question of prices depends very largely, of course, on costs, and in the following discussion I shall have occasion to refer frequently to the costs of the Boston Edison Company, since I shall devote my attention almost exclusively to the prices of that company. The electric light companies of this state are, as you know, under the control of the Gas Commission and make very full reports to that commission, in addition to which all the financial and engineering operations of the companies are open to the inspection of the commission. Out of the reports to the commission the latter makes public only some of the figures; and since it would be obviously improper for me to make public what the commission does not, I wish it clearly understood that in the following discussion any figures that are not taken from the Gas Commission report are used for illustration merely and do not represent actual results.

Beginning now with the total costs, the total costs for a year are

[1] An address delivered before the Senior Class in Electrical Engineering of the Massachusetts Institute of Technology, in May, 1905, and May, 1906.

Since the above was written the Edison Company has made changes and reductions in its rates, particularly to its small consumers; but these changes affect only the figures and not the principles.

easily taken from the report; and for the report of the year covered by the last published report of the commission the total income of the Boston Edison Company was $2,700,000, which just paid all the cash outlay, a small depreciation charge, and a net dividend of 5 per cent. on the $200 per share paid in on the stock. In other words, $2,700,000 was the total cost of the current sold and service rendered by the Boston Edison Company; and if a single payment were to be made for the current and service, the proper price would have been, as it was, $2,700,000. The question of the total cost is simple, and the question of the total of the prices is likewise simple; it is the question of the division of the amount among the different customers that constitutes the price question. The solution from a scientific point of view is for an electric company simpler than for most businesses, as may be brought out by a homely though amusing illustration.

Suppose a farmer buys a calf for $9, spends $1 worth of his time in killing and skinning it, and then starts to figure out what is the proper price at which he should sell the veal and the price at which he should sell the hide. The farmer does not have to consider the question from a scientific point of view. He merely sells the hide and the veal for what he can get, and for the most he can get; and if he could get $15 for the hide and $20 for the veal, he would take them without a qualm of conscience or any idea that the commissioner of agriculture might hold a hearing as to reducing his prices or determining the fair market value of his farm. Public service corporations, however, receive a limited monopoly from the public, and in return for that monopoly are expected to sell what corresponds to their veal and hide at fair prices. It should be noted, however, that this requirement of fair prices should extend only to the extent of the monopoly granted. If a public service corporation has two products, in respect of only one of which it is granted a monopoly, then the public has a right to control only the prices of the monopolized product, and in respect of the product for which the public grants no monopoly the public has no right to determine prices. This rule, of course, is clear.

Returning now to the Boston Edison Company, the total cost of its current and service was $2,700,000, and the $2,700,000 received was a fair price; but not only is it necessary that the total price should be a fair one, but it is also necessary that the division of the price among the different customers should be a fair one. In fact, this is the most necessary feature, since it does not affect a business man

very seriously to pay an extra charge of 10 per cent. provided his competitor likewise pays the same extra charge; while if a business man pays only a fair charge, but his competitor gets a 10 per cent. rebate, then the first customer is worse off in spite of the fact that in this case the seller is getting even less than a fair price, while in the other case the seller was getting an unfairly high price.

Now how is the $2,700,000 which it costs the Boston Edison Company to be divided up among its customers? It supplied about 12,600 customers in all, making the average about $200 per customer. It supplied about 900,000 lamps, or their equivalent in other service, making the cost $3 per lamp. It supplied about 25,000,000 kilowatt hours, making the cost about 10 cents per kilowatt hour. While these are the average costs or average prices per customer, per lamp, or per kilowatt hour, it is perfectly clear that we cannot depend solely on averages in any particular case, any more than any of you expect to work for the average earnings per adult male in the state of Massachusetts. The average cost per customer of the Boston Edison Company is about $200, but some customers cost very much more and some very much less. The average cost per lamp is about $3, but some lamps cost much more and some much less. The average cost per kilowatt hour is about 10 cents, but some cost much more and some much less.

Now what is the theory that determines the proper unit of charge for a public service corporation? The earliest public service corporations in the modern sense were probably the toll roads and bridges; the first made a charge varying with the distance traveled and the bridges made a charge depending chiefly on the weight, though both were so arbitrarily made up that no very definite rule can be discovered. The water companies, which were also some of the earliest public service corporations, began by making the charge proportional not to the amount of water or value of service rendered, but proportional to the value of the land or house to which the water was supplied; and while this method has continued even to the present time, the tendency is now in the line of making the water charge proportional to the number of fixtures that can use water and to the quantity of water used. It should be noted, however, that the tendency towards meter rates for water is only in part because this is considered a fair method in itself, but is partly because no other method prevents waste.

The comparison between roads, bridges, and sewers (which are always considered proper subjects of municipal enterprise), water sup-

ply (which is often so considered, but is carried on successfully by private enterprise), gas and electricity (which are usually best done by private enterprise, but occasionally well done by the public), and such enterprises as municipal ice or municipal contracting or municipal houses (which, as we know, have always proved failures) may perhaps indicate a guiding rule. For roads and bridges the public intends that no charge shall be made, but that they shall be free to every one. Under these circumstances they are successfully carried on by the public.

The public intends that every one shall have water, with no charge except such as is necessary to prevent waste. Under these circumstances the work is usually, though not always, well done by the public. The public intends that every one who wants them shall have gas and electricity at a fair price proportional to the cost of the service, and these businesses are occasionally well done by the public. I presume that the public also intends that every one who wants food or houses or clothing shall have them at a fair price; nevertheless the public for some reason does not feel the necessity so strongly as in the case of roads or bridges or water, and the supply of food or clothing has been carried on by municipalities successfully only in times of great stress. In other words, successful instances of municipal management have almost invariably been cases where the municipality wished to supply the product free or at less than cost, as in the cases of bridges and water or of food at times of famine, and the instances of a municipality successfully engaging in genuine trading for profit have been very rare.

This discussion as to the proper limits of municipal trading has taken me away from my subject, which was the question of what is the proper basis or unit of charge for an electric light company. There is no essential reason why either the kilowatt hour or its multiples or submultiples, the lamp hour or horse-power hour, should have been used. The telephone companies and some water companies charge so much per customer, but by a graded differential system they take account of the fact that some customers cost them more than others. In the old days the electric companies charged so much per lamp (usually $12 per annum) and some electric companies and some water companies do so still, the water company's charge being so much per fixture. In all these cases, however, the companies (or municipalities, when the supply was municipal) have by various systems of differential

charge recognized the fact that some telephones or customers or lamps or fixtures cost them more than others.

I will not go into the history and science of electric supply to explain why it is that most electric companies have finally settled on the kilowatt hour or its equivalents — the lamp hour or horse-power hour — as the basis of charge; in fact, I could not, since this has come about more as a matter of growth than from any well-defined plan or reason; but I do wish to state most emphatically that there is just as much reason for differentiating between the kilowatt hours that cost the company 20, 30, and 50 cents each, and even more, and the kilowatt hours that cost the company less than one-half cent each as there is between customers and lamps. We supply some customers at $12 each per annum and charge some customers $40,000 each per annum, and we intend that each of these customers shall give us a fair margin of profit, if we can get it, and shall in no case be supplied at a loss. We supply some lamps at a cost of $1 per annum each, and even less, and get as high as $10 or $15 per annum from others, and again intend that they shall all give us, so far as possible, a fair margin of profit, and that none shall be supplied at a loss. We supply some kilowatt hours at 20 cents and some at 2½ cents; and while we try to get a fair margin of profit on them all to pay our 5 per cent. dividend, yet we actually lose money on a great many of the kilowatt hours we supply at the highest prices.

Now how do we distinguish between the kilowatt hours that cost 20 or 30 cents and those that cost only one-half cent? In the case of a customer we have a definite address or location, and know exactly what happens when he comes on to the system and uses current. In the case of different lamps we know very clearly that to supply one lamp for a year takes only 60 pounds of coal and to supply another over half a ton, so that the first lamp may be supplied at the cost of half a ton of coal cheaper than the second if the other expenses are the same. The kilowatt hour, however, while more exact and definite than the customer or the lamp, is more a definition than a concrete quantity, and the variation in the cost must be considered more carefully.

In the general analysis of rates, which has been my particular work with the Boston Edison Company for the last few months, I have a great many methods of analysis, but I can perhaps make the matter clearer to you in this short talk by explaining what we have been doing lately in the case of a very large customer who was desirous of taking current

from us. This particular customer has the equivalent of 10,000 to 15,000 lamps connected, of which he will probably use about 8,000 at any one time. To supply him, therefore, we shall have to assign about one-tenth of one of our new turbines, together with the proportion of the steam piping, boilers, pumps, condensers, coal handling apparatus, and station building, also switchboard at the L Street Station, high tension cable from L Street Station to switchboard in Boston substation; at this substation storage battery, and underground cable and duct from the substation to this particular customer. In this particular case most of this apparatus has been already ordered in anticipation of the regular growth of business; but when this customer comes on and uses the proportion of the turbine, boilers, etc., no one else can use them at the same time, hence we must get from this particular customer each year the depreciation and the interest or dividends on their cost, since, of course, the electrical companies do not sell us dynamos nor the boiler companies boilers for nothing, and our stockholders do not give us money to pay for them unless they are assured of a reasonable return on their investment, which, as you know, has been only 5 per cent. for some years.

In addition to the interest and depreciation, and by the way taxes, which last year amounted to over 33 per cent. of the money we paid our stockholders, there are various other expenses which will be increased when we get ready to supply this new customer. We must keep the steam pipes hot from the boilers to the turbine even when no current is being turned out from the dynamo. We must keep two men by the turbine all the time to watch it and keep it oiled. We must keep a water tender at the boilers to see that the water does not get low in the boilers and cause trouble. We must keep men by the switchboard all the time to adjust the pressure that the lamps may neither be dim nor burn out, and there are various other expenses that will be required to get ready and keep ready to supply this customer even if no current be passing out over the lines. I will not describe all these expenses, because this paper is not on the subject of costs, but on the methods of making prices. I may say, however, that we figure that it will cost us, including the interest and depreciation on the plant required and the other expenses, something like $24,000 per annum merely to keep ready to supply this customer, and unless we get this sum for the keeping ready of this machinery we are out of pocket.

Now let us see what the cost is per kilowatt hour. First, let us take

a case so extreme as to be absurd but nevertheless instructive, and suppose that this customer used just one kilowatt hour. We may neglect the amount of coal used for one kilowatt hour, and we find that the total cost of that kilowatt hour was $24,000. Let us, however, take an extreme but not an absurd case, and suppose that this customer had his own plant but wanted central connection from us in case of a breakdown, and during one week of the year he shuts down his own plant and uses 24,000 kilowatt hours from us. The cost of the coal to us will be, we hope, something like one-half cent per kilowatt hour on our new turbine plant, and the coal for these 24,000 kilowatt hours will therefore cost us something like $120. Adding this to the $24,000 per annum that we pay for keeping ready and dividing by the kilowatt hours actually used, we find the cost a little over $1 per kilowatt hour.

Now take an ordinary case, a case similar to many we have on our books of other customers, and suppose that this customer should use his light about one hour per day and should use about 116,000 kilowatt hours. The cost of these for coal and for the renewal of the incandescent lights when they get dim or the trimming of the arc lights would be about $2,400, making the total cost, including the $24,000 per annum for keeping ready, about $26,400, or about 17 cents per kilowatt hour.

Take still another case, and suppose this customer used his lights about ten hours a day, say 1,200,000 kilowatt hours in all. Adding the cost of the coal and lamp renewals to the cost for keeping ready and dividing by the number of kilowatt hours, we find the rate to be about 3.2 cents per kilowatt hour; and of course if the customer should use his lights twenty-four hours per day the cost per kilowatt hour would be lower still. The above analysis has been for a customer with sufficient lamps to require one-tenth of one of our turbines. It is, however, perfectly obvious if we consider a customer who only requires one ten-thousandth of one of the turbines, say a customer with ten or twelve lamps, that the cost to him will be in the same proportion and the same per kilowatt hour as in the case of a large customer.

In addition, however, to all the expenses I have outlined that are actually increased every time a customer comes on our line there are a great many other expenses; for instance, when we lay a main in a street we have at first only one or two customers on the street, and these perhaps use only 1 per cent. of the whole capacity of the main. It would be bad engineering to put in a main so small that whenever a customer

came on it had to be dug up and replaced by a larger one; and yet the excess cost of the large main put in looking towards the future growth can hardly be charged to the particular customer who uses it first, but must be spread over the whole business, or rather charged to those customers who on the whole get the benefit.

Another expense of this nature is the fact that many of our engines are of older type than the modern turbine and involve considerably higher coal and labor cost. In our work we aim at keeping the total expense at a minimum. If we should throw away these old engines and put in turbines we could reduce our coal expense, but would increase our depreciation charge by an even greater amount; hence we run the old engines until we can afford to scrap them. But it would not be fair to charge the extra coal cost due to running these engines only to the old customers, for whom these engines were put in, and to give the whole advantage of the turbine to the new customers of this year; hence this extra cost forms an item which must be distributed over the whole business and cannot be ascribed to any particular customer. When the city of Boston abandons a street and makes us abandon our conduits without compensation, that again is an expense that cannot be ascribed to any particular customer. Besides these three sample cases there are many similar expenses; and without going into all of them in detail I may say that about half of the money that we collect from our customer goes towards paying expenses that cannot be said to be incurred for the benefit of any particular customer to whom they can be directly charged, but are incurred for the general good of all our customers, and are incurred most of all for the benefit of the small customers reached by our great network who could have the benefit of our supply, or rather of any supply of electricity, in no other way. In other words, half our expenses are for items that are for the general good of the city or of all our customers and that cannot be charged to any particular customer. Hence if a customer actually increases our expenses by say $10 we should, provided of course that he benefits by all our expenses, charge him a total of $20 as his fair share of all our expenses; and if he increases our expenses directly, by say $1,000, we should charge him a total of $2,000. If he increases our expenses by 17 cents for each kilowatt hour that he uses then we ought to charge him 34 cents per kilowatt hour in order that he may pay his fair share of our total expenses, and if he increases our expenses by 4 cents for each kilowatt hour that he uses then we ought to charge him 8 cents.

The difference between our increase of expense when such a customer comes on is of course not our profit, but is merely the proportion of our other expenses that such a customer should bear.

Unfortunately our prices were established before we knew just what the product was going to cost us, and we established a maximum price of 18 cents per kilowatt hour, much like the old woman who had a cow and a hen and tried to sell them for an average price of $15 each. She sold the cow all right, and we sold a great many kilowatt hours at 18 cents for which we ought to have had a much higher price. We also, because the art was new, sold some kilowatt hours at 18 cents for which we ought to have charged only 8 cents or so, and the profit on these made up for the loss on the other.

The case, however, was not and is not quite as bad as I have made out for the following reason. It is the customer who uses his lights and our machinery only a short time that costs the high amount per kilowatt hour; and when we have many such customers we find that, though nearly all of them use their lights at our peak, between four and five P.M. in the winter, there are some of them who use the lights at other times than this and do not use them at the time of the peak. Hence for short-hour customers we find we can, to a small extent, use the same machinery twice and get extra income, so that, allowing for this fact as worked out from our records, we find that a price of 20 to 25 cents would be a fair price for these short-hour customers. Nevertheless we have to keep our price down to 18, for if we should try to raise it we should have a row beside which Mr. Hearst's attempt at 80 cent gas would look like an editorial in the Boston *Transcript*. We can sell at 18 because this gives us a margin over the bare increase in expenses; but the customers who pay us 18 cents do not pay their fair share of our whole expenses and are among the least profitable of our customers.

If, however, a customer uses his lamps about one and one-fourth hours per day and pays us at the 18 cent rate, he pays us the cost of keeping ready to supply him; and after we are paid for the cost of keeping ready the cost to us of additional current is only the cost of the coal and lamp renewal and also an amount that we must allow to take account of the fact that while we can often sell the use of the same machinery twice to short-hour customers, yet long-hour customers are sure to use our machinery at the same time and must therefore be charged the full amount for the use of the machinery. To a customer who has used our machinery for a little over an hour a day at the

18 cent rate we therefore sell any additional current he may use at a lower rate.

If we made out our bills once a year the determination of the exact figures of hours and rates would be fairly simple; but as a matter of fact we render bills monthly, partly because we have some customers that we cannot trust for more than a month, but chiefly for the reason that our customers prefer monthly settlements. Now the fact that a customer in some months uses enough current at the 18 cent rate to pay us the cost of keeping ready in that month will not prevent his being a loss to us in some other month when he does not use enough current to pay even the cost of keeping ready. The fact that residences in the Back Bay use a good deal of current in the winter months does not prevent our having to pay interest and depreciation on the Back Bay investment in the summer months when the houses are closed. In order to allow for this we do not give the lower rate until the customer has used his lights and our machinery a little longer than enough to pay us the cost of keeping ready that month, and we make the low rate higher than would otherwise be necessary.

The exact figures we have adopted are that up to a use of from thirty to sixty hours per month, according to season, and totalling 520 hours per year, or about one and one-half hours per day, the rate is 18 cents and for any additional current only 12 cents.

The amount of our machinery that the customer uses is determined each month by an instrument called a demand indicator, or we often call it a discount indicator, because it indicates the point at which the discount from the 18 to the 12 cent rate begins.

Personally I do not think this monthly determination is the correct method, but that we ought to determine the amount of our machinery that the customer uses each year, since our business is a yearly one and the fact that our machinery is not used in summer does not save us any appreciable amount in our cost of keeping ready. I think it very probable that in the future we shall change this and take the reading of the discount indicator only once a year. This change will involve a reduction in the rate; otherwise taking the reading of the discount indicator yearly might result in increasing the bills.

The reason we make the time during which the 18 cent rate is charged 520 hours and the secondary rate 12 cents is in order to get a little profit in some months to make up for the months in which a customer fails to pay us even the cost of keeping ready to supply him.

If, however, a customer is a steady customer and every month uses enough current at the 18 cent rate to pay us this cost, then we are getting more out of him than we need and we say to such customer, "If you will *guarantee* to use your lights and our machinery for 400 hours and pay us at the rate of 20 cents (a less total than 18 cents for 520 hours), then we will give you the rest of your current at 8 cents." It would be simpler, of course, if the primary rates could have been uniform, *i. e.*, either 18 cents or both 20 cents. When we adopted this contract we had hopes that some day we might make the standard rate 20 cents, reducing the low rates still lower to balance it, but this is still a problem of the future.

In these contracts we take the yearly determination of the amount of machinery the customer has required us to keep ready for him, but we allow once a month that the customer can use an excess without charge, *i. e.*, once a month we permit the indicator to be cut out. The reason for this is that we can count that so few of these unusual demands will come at the time of our peak that we can afford to give our customers this privilege.

Our retail prices are therefore divided into two classes: non-contract, where a customer guarantees nothing and is usually a loss to us in some months, and contract rate, where a customer guarantees to use enough current at the high rate to insure us against loss and therefore gets the remainder of his current at a very low rate.

In addition to our retail rates we have wholesale discounts, and before describing how we make them I will explain why we make them. There is, of course, a difference in cost between supplying a large and a small customer, and the difference in cost as nearly as we can calculate is the same as the discounts we allow. The reason for this is that many of the special expenses that I spoke of before cannot be ascribed to any particular customer, yet we do know that they are not part of the cost of supplying certain classes.

The cost to us of supplying current in large quantities is considerably less than our average costs, since to supply all our customers we have to maintain a great network of mains; and incidental to this there are many expenses that are needed when we have many small customers, but are not needed when we supply the same quantity of current wholesale.

Since certain items of our expense are needed for small customers solely, on figuring the cost of supplying a large customer we do not

and should not include these expenses. For instance, when the city makes a change in a street and writes us to move our conduits at a large expense, the small customer says to us, "I must have electricity from you and am willing to pay my share," but the large customer says to us, "I can make electricity myself rather than pay the cost of moving the conduit."

It is clear, therefore, that moving this conduit is a part of our cost of supplying small customers and is not a part of our cost of supplying the large customer. The large customer may use the conduit; yet so long as the use of the conduit for the large customer does not add anything to the costs, it is clear that we cannot and ought not to try and make the large customers pay an expense not for his benefit, an expense that is incurred solely for the benefit of the small customers. Of course we should make our large customers pay every single expense that is incurred for their benefit; and if the conduit is in any degree for the benefit of the large customer, then to that extent and no more the large customer should pay.

Our wholesale discounts, therefore, are arranged to give our customers a rate in proportion to the cost to us to supply them. It is true that for large customers this is less than our average rate and average cost; but it should be kept clearly in mind that the small customer loses nothing in any way by the fact that the wholesale rate and wholesale cost to large customers is less than the retail rate and retail cost, and that the use of certain of our facilities by large customers at less than the average price does not add anything to the expense of supplying small customers.

The big department stores get no special advantage in competing with the small store by reason of our low wholesale cost for current, since the large stores already have the advantage of being able to put in a plant.

For the amount of current that would be used by a large customer who gets our wholesale discounts the cost of making so large an amount of current for himself in an isolated plant would be only 10 or 15 per cent. greater than our price to him. At first sight, therefore, it might seem that this 10 or 15 per cent. represents an advantage that the wholesale customer gets, as compared with his small competitor, over what he would get if we refused to supply him.

However, the wholesale customer gets his current we will say 15 per cent. cheaper than if we refused to supply him. If the retail customer

had to make his small amount of current for himself it would cost him, not 15 per cent., but 100 per cent. more than our price, so that the retail customer gets 100 per cent. and the wholesale customer only 15 per cent. advantage from the fact that the Edison Company exists.

Even take the worst case and suppose that we refused to supply the wholesale customer and did supply the retail customer. Even in this case the loss of the wholesale business would not decrease our expenses in proportion to the decrease in income, because the income is expected to be in excess of the expenses; so that if we lost the wholesale business, even at the present low rate, the cost of the retail business would be increased by the amount of the loss on the wholesale business, which would be much more than 15 per cent., and the small store would be more handicapped in competing with the large store than it is now.

I trust, therefore, that it is clear that our making all our prices, including our wholesale discounts, proportionate to cost is to the advantage of small customers as well as to the advantage of large customers.

The way we give the wholesale discounts to large customers is to give a discount of 40 per cent. on the excess of the monthly bill above $150, and 50 per cent. on the excess above $550. In this way we charge to the large customers some share of all these special expenses that are incurred for the benefit of our customers generally and small customers in particular, since on the first $150 of their bill they pay exactly the same rate per unit as the small customers. On the balance of the bill they get a discount to take account of the fact that a large proportion of our expenses is not incurred for them.

The reason for making the discounts on the excess of the bill rather than on the whole bill is to prevent the customer from saving money by wasting our current. If the discount is made say 20 per cent. on the whole bill whenever the bill gets to $200, then a bill of $199 gets no discount, while the use of a little more current gives a bill of $200, which is $180 net. On the plan of giving discount on the excess only we give 40 per cent. on the excess over $150, so that this feature of the customer's saving money by wasting current never enters.

It is important to note that the difference between our two methods of discounts is only in kind; they are both based on cost.

Our long-hour discounts are given because of the difference in cost. A long-hour customer costs us less per kilowatt hour than a short-hour customer; and we charge him less because, while he may use the same amount of machinery, which represents the larger element of cost, he

uses a larger amount of current, which represents the small element of cost, thus reducing the average cost per kilowatt hour used.

The wholesale discounts also depend on cost. A large customer costs us much less per kilowatt hour, or per kilowatt, than the equivalent number of smaller customers, and we charge them all in proportion to cost.

I will next speak of our minimum charge of $1 per month, which is a very interesting application of the same principle as that on which our wholesale discounts are based. For very small customers the cost of installing the service and meter and maintaining and reading the meter and making out and posting the bills and keeping the accounts comes to a very considerable sum in proportion to the cost of current alone, and amounts to about $8 per customer per year. Hence if a customer uses no current at all and we keep no machinery ready for him, nevertheless it costs us $8 to keep his meter there, and he ought to pay us $8 meter rent besides what he ought to pay us for his current. If we tried to charge this $8 in addition to the charge for current it would make the cost so high that these small customers would use no current at all. In these cases, therefore, as in the case of the big wholesale customers, we do not even attempt to collect from them the proportion of all our expenses, but only those expenses that are incurred for their benefit, and sometimes not even those. We cannot do this exactly, but the $1 per month minimum is the nearest we can come to it. If a customer uses no current at all he costs us $8, without reckoning the expense of the investment at his disposal, and we get $12. If a customer uses just $1 worth of current each month he costs us $8 for the meter, and his use of current adds $6 to our expenses that we would otherwise have to incur anyway, making a total of $14; and he pays us $12, or an actual loss of $2, not reckoning interest or depreciation on plant, etc.

If he uses $20 worth of current it adds to our expenses about $18 in all and we get $20, or only $2 towards our other special expenses, like moving conduits, etc., instead of $10, which would have been his fair share.

Besides our general rates for lighting, which I have described above, we have a special rate for power, because it can be supplied cheaper than light, a special rate for churches, which is a charity, and a rate for Central Station connection to isolated plants. We also have a price intermediate between our large wholesale discounts, which I have described, and the retail prices. I will not take up your time with these

various details of our large system because they are either founded on the principles of our regular rates or else they are excrescences on our system that we are going to get rid of as soon as possible.

Before closing I wish to say two things more and hope they will be of value in guiding any discussion. First, this paper is a paper on the principles and methods of making prices and not a paper on costs, and I have not tried to give exact costs.

Second, as to the complications of such a system of prices as I have outlined. I was responsible for the introduction into this country of the Wright demand system of charging, on which the Boston Edison system is based, and have therefore heard a great deal about complication; but these systems are not as complicated as the United States Postal System, if one should attempt to explain the reasons why first-class rates should be exactly thirty-two times as much as second-class, etc.

They are not as complicated as the Boston water rates.

They are not as complicated as telephone rates.

They are not as complicated as railroad rates and classification.

They are not as complicated as a contractor's rates for excavating or piling or doing any work, unless he is allowed to make a guess and lump his estimates. I do not mean that one bid of a contractor may not be simple for excavating or other work, but you have no assurance that his next bid for the same work may not be higher or lower, or that his bid for similar work will be in the same proportion.

The only kinds of prices that are as simple as Boston prices for electricity are such as the price of Governor Douglas's $3 shoes, which are sold in a single quality and at retail only.

Before any one calls Boston Edison prices for electricity complicated I will ask him to name an article that is sold both wholesale and retail in qualities whose costs vary by several hundred per cent., an article that the customer may take delivery of at any time and in any amounts that he wishes, an article whose price is made so that the price will stand for several years without change, and whose price is not far more complicated than Boston Edison prices for electricity.

It would be possible, of course, to make our prices more simple, and in some directions we hope to simplify them later, but if we made our prices too simple they would be unfair, just as a hotel's prices would be unfair if it charged the same price for a boiled egg and a Porterhouse steak. A simple article like copper can have a simple price, but a complicated service like a railroad or a hotel or an electric service must have a complicated price in order that the price may be fair.

TENSION TESTS OF STEEL ANGLES WITH VARIOUS TYPES OF END-CONNECTION[1]

By FRANK P. McKIBBEN

THE tension tests which form the subject of this paper were made in the testing laboratory of the Massachusetts Institute of Technology

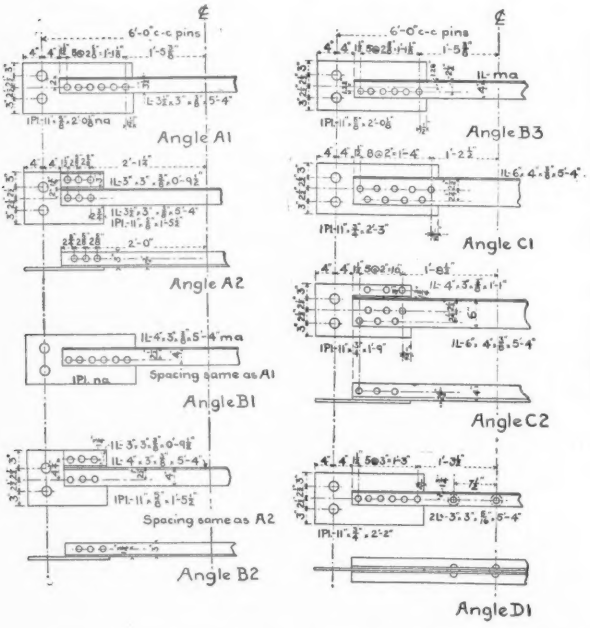

FIG. 1.—TENSION TESTS OF STEEL ANGLES

(Nine Types of End-Connection Tested)

NOTE.—All angles had both ends alike. All angles 5 ft. 4 ins. in length. Rivets, $\frac{7}{8}$-in. Holes punched, $\frac{15}{16}$-in. Pin holes, 2-in. diameter drilled.

upon twenty-seven specimens of rolled steel angles, such as are used for tension members in riveted structural work. They were made with a view of studying the following points:

1. The ultimate strength of the angles in tension.

[1] A paper read before the American Society for Testing Materials at Atlantic City, N. J., June 23, 1906. Reprinted from Engineering News, July 5, 1906, **56**, No. 1.

2. The value of a lug in transmitting stress from the outstanding leg of the main angle into the hitch plate.

3. The relative strength of angles where the gauge line for rivets and where the centre of gravity line, respectively, pass through the centre of the pull.

4. The relative strength of single angles and angles riveted together to form pairs.

There are three specimens of each of nine different types, making in all twenty-seven specimens. These are shown in detail in Figure 1. Each of the main angles, 5 feet 4 inches in length, is riveted at each end to a hitch plate.

Types A_1, B_1, and C_1 consist each of one angle, $3\frac{1}{2} \times 3 \times \frac{3}{8}$ inches, $4 \times 3 \times \frac{3}{8}$ inches, and $6 \times 4 \times \frac{3}{8}$ inches, respectively, riveted to the hitch plates by one leg only.

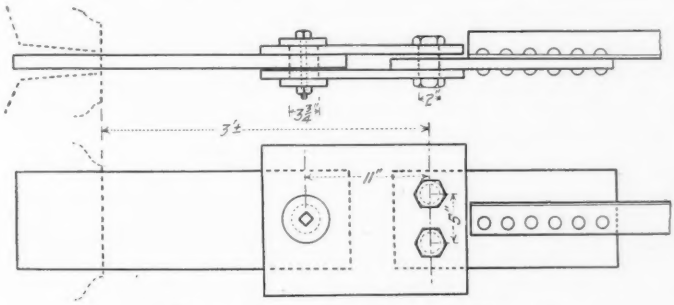

FIG. 2.—TENSION RIGGING FOR TESTS OF STEEL ANGLES

Types A_2, B_2, and C_2 consist each of one angle of the same size as A_1, B_1, and C_1, respectively, and have both legs connected to the hitch plates, the outstanding leg being connected by means of a lug angle.

Each specimen of types D_1 and D_2 is made up of two $3 \times 3 \times \frac{5}{16}$ inch angles, one on either side of the hitch plate. D_1 is not, and D_2 is, provided with lugs for each of the outstanding legs of the main angles.

In each of the types just mentioned the gauge line for rivets in the main angle is run through the centre line of pull. In the case of angles with unequal legs the long leg is placed in contact with the hitch plates.

Type B_3 consists of one $4 \times 3 \times \frac{3}{8}$ inch angle connected to the hitch plates by one leg only. It differs from type B_1 in that the line of pull coincides with a projection of the centre of gravity line instead of with the gauge line for rivets.

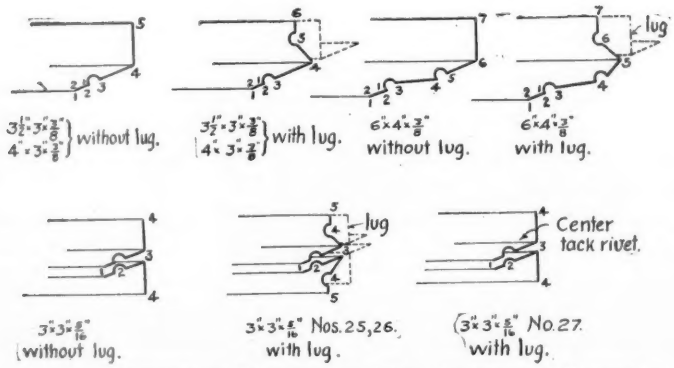

FIG. 3.—SKETCHES OF FRACTURES OF STEEL ANGLES WITH VARIOUS TYPES OF END-CONNECTION

(Small figures at fracture indicate origin and progress of rupture)

The end-connections were designed to insure failure in the main angles, and the specimens were made as long as could be tested conveniently. The hitch plate at each end of each specimen was provided with two 2-inch holes, by means of which it was pinned between two holding plates, fastened in turn by a single pin to a third plate gripped by the testing machine. A diagram of this holding device is shown in Figure 2.

All of the pieces of angles of a given size were cut from one long angle, and from each of these long pieces there were made also two small tensile test specimens. Table I gives the average results of the tensile tests on the small specimens, which were approximately $18 \times 1\frac{1}{2} \times \frac{3}{8}$ or $\frac{5}{16}$ inches in size.

TABLE I—TENSILE STRENGTH OF SMALL TEST SPECIMENS CUT FROM STEEL ANGLES

Size of angle from which specimen was cut	$3\frac{1}{2} \times 3 \times \frac{3}{8}$ inches	$4 \times 3 \times \frac{3}{8}$ inches	$6 \times 4 \times \frac{3}{8}$ inches	$3 \times 3 \times \frac{5}{16}$ inches
Yield point, pounds per square inch . . .	33,160.0	31,600.0	32,600.0	34,800.0
Ultimate strength, pounds per square inch	59,300.0	54,000.0	51,600.0	61,000.0
Elongation, per cent. in 8 inches	28.0	28.6	31.1	29.5
Reduction of area, per cent.	48.9	54.6	56.5	52.6
Appearance of fracture	Silky	Silky	Silky	Silky

Figure 3 shows diagrammatically the outlines of the various fractures, all of which occurred in the main angles. There was no failure of rivets. The numbers on the sketches show the sequence of the

fractures. With the exception of one of the specimens, made of two $3 \times 3 \times \frac{5}{16}$ inch angles, failure took place at one of the inner rivets which connects the angle to the hitch plate — that is, the connecting rivet which lies nearest the centre of the specimen. In the case of the exception noted rupture occurred at the centre of the specimen, where there is a single rivet connecting the two angles together. In all cases, just before failure the metal between the inner rivet and the outer edge of the leg connected by that rivet to the hitch plate drew down considerably at both ends of the specimen. Failure then occurred

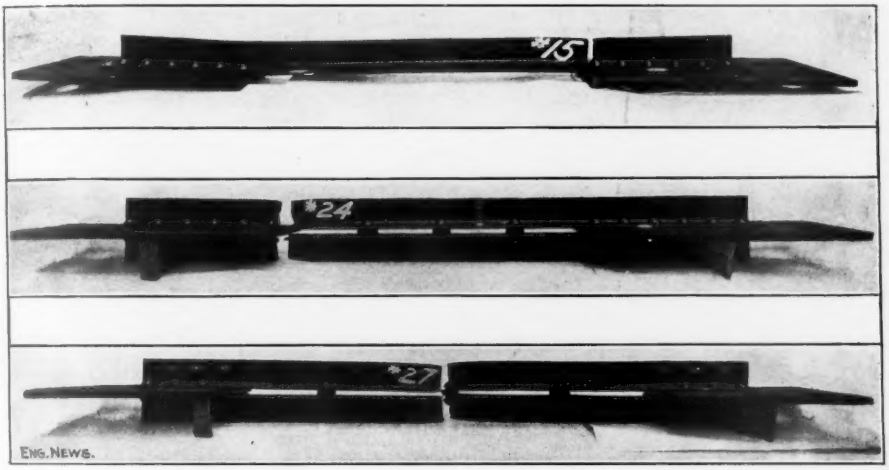

FIG. 4. — VIEWS OF THREE OF THE TEST SPECIMENS AFTER FRACTURE
(No. 27 was the only specimen which did not break at the end-connection)

at this point, continuing slowly across the horizontal leg and then up the vertical leg. With the one exception cited, failure occurred, in all specimens having lugs, on a zigzag section passing through rivets in the horizontal and in the vertical legs. In order to secure the greatest strength from an angle in tension this zigzag section should be equal to or greater than the net right section. In none of the specimens tested is this the case. Consequently the total ultimate strength of some of the specimens with lugs is less than that of similar specimens without the lugs. However, the strength per square inch of net area is greater where the lugs are provided, showing that with the proper spacing of rivets to utilize the maximum net area the lug is an advantage.

Table II shows in detail the results of the tests. Table III shows the per cent. increase in the strength per square inch of net area due to the lugs.

TABLE II — SUMMARY OF TENSION TESTS ON STEEL ANGLES

Type.	No. of specimens.	Nominal size.	Cross Section. Area in Square Inches.			Breaking Load.		Strength of material developed.[1]	Remarks.
			Nominal.	Actual gross.	Net.	Total.	Per square inch of net area.		
						Lbs.	Lbs.	%	
A_1	1	$3\frac{1}{2} \times 3 \times \frac{15}{16}$	2.30	2.29	1.95	89,500	45,900	77.4	Without lugs
A_1	2	$3\frac{1}{2} \times 3 \times \frac{15}{16}$	2.30	2.32	1.98	96,100	48,500	81.8	
A_1	3	$3\frac{1}{2} \times 3 \times \frac{15}{16}$	2.30	2.35	2.00	95,200	47,600	80.2	
A_1	Mean	$3\frac{1}{2} \times 3 \times \frac{15}{16}$	2.30	2.32	1.98	93,600	47,400	79.8	
A_2	4	$3\frac{1}{2} \times 3 \times \frac{15}{16}$	2.30	2.28	1.78	84,600	47,500	80.1	With lugs
A_2	5	$3\frac{1}{2} \times 3 \times \frac{15}{16}$	2.30	2.28	1.78	88,600	49,800	84.0	
A_2	6	$3\frac{1}{2} \times 3 \times \frac{15}{16}$	2.30	2.27	1.77	91,200	51,500	86.8	
A_2	Mean	$3\frac{1}{2} \times 3 \times \frac{15}{16}$	2.30	2.28	1.78	88,100	49,600	83.6	
B_1	7	$4 \times 3 \times \frac{15}{16}$	2.49	2.44	2.10	85,000	40,500	75.0	Without lugs
B_1	8	$4 \times 3 \times \frac{15}{16}$	2.49	2.42	2.09	84,000	40,100	74.3	
B_1	9	$4 \times 3 \times \frac{15}{16}$	2.49	2.50	2.15	85,600	39,800	73.7	
B_1	Mean	$4 \times 3 \times \frac{15}{16}$	2.49	2.45	2.11	84,900	40,100	74.3	
B_2	10	$4 \times 3 \times \frac{15}{16}$	2.49	2.42	1.92	83,500	43,500	80.5	With lugs
B_2	11	$4 \times 3 \times \frac{15}{16}$	2.49	2.43	1.92	85,100	44,300	82.0	
B_2	12	$4 \times 3 \times \frac{15}{16}$	2.49	2.45	1.95	84,100	43,100	79.9	
B_2	Mean	$4 \times 3 \times \frac{15}{16}$	2.49	2.43	1.93	84,200	43,600	80.8	
B_3	13	$4 \times 3 \times \frac{15}{16}$	2.49	2.41	2.07	88,600	42,800	79.3	Without lugs
B_3	14	$4 \times 3 \times \frac{15}{16}$	2.49	2.42	2.09	90,400	43,200	80.0	Centre of gravity line through pull
B_3	15	$4 \times 3 \times \frac{15}{16}$	2.49	2.41	2.07	91,000	44,000	81.4	
B_3	Mean	$4 \times 3 \times \frac{15}{16}$	2.49	2.41	2.08	90,000	43,300	80.2	
C_1	16	$6 \times 4 \times \frac{15}{16}$	3.61	3.53	3.11	131,000	42,100	81.6	Without lugs
C_1	17	$6 \times 4 \times \frac{15}{16}$	3.61	3.54	3.12	125,700	40,300	78.1	
C_1	18	$6 \times 4 \times \frac{15}{16}$	3.61	3.50	3.07	128,200	41,800	81.1	
C_1	Mean	$6 \times 4 \times \frac{15}{16}$	3.61	3.52	3.10	128,300	41,400	80.3	
C_2	19	$6 \times 4 \times \frac{15}{16}$	3.61	3.50	3.04	131,500	43,300	84.0	With lugs
C_2	20	$6 \times 4 \times \frac{15}{16}$	3.61	3.50	3.03	130,200	42,900	83.2	
C_2	21	$6 \times 4 \times \frac{15}{16}$	3.61	3.50	3.04	131,900	43,400	84.1	
C_2	Mean	$6 \times 4 \times \frac{15}{16}$	3.61	3.50	3.04	131,200	43,200	83.7	
D_1	22	Two $3 \times 3 \times \frac{5}{16}$	3.56	3.44	2.88	134,100	46,600	76.4	Without lugs
D_1	23	Two $3 \times 3 \times \frac{5}{16}$	3.56	3.43	2.87	136,500	47,700	78.3	
D_1	24	Two $3 \times 3 \times \frac{5}{16}$	3.56	3.49	2.91	139,100	47,800	78.4	
D_1	Mean	Two $3 \times 3 \times \frac{5}{16}$	3.56	3.45	2.89	136,600	47,400	77.7	
D_2	25	Two $3 \times 3 \times \frac{5}{16}$	3.56	3.43	2.69	137,900	51,200	84.0	With lugs
D_2	26	Two $3 \times 3 \times \frac{5}{16}$	3.56	3.43	2.69	140,400	52,200	85.6	
D_2	27	Two $3 \times 3 \times \frac{5}{16}$	3.56	3.42	2.86	138,800	48,500	79.6	
D_2	Mean	Two $3 \times 3 \times \frac{5}{16}$	3.56	3.43	2.75	139,000	50,600	83.1	

[1] Figures of previous column compared with specimen tensile test results of Table I.

The results of the tests show that the ultimate strength per square inch of net section for angles having gauge lines for rivets passing through the centre of pull varies, for the single angles, from 39,800 to 51,500 pounds, which is approximately from 74 per cent. to 87 per cent. of the strength of the tensile test specimens; and for angles

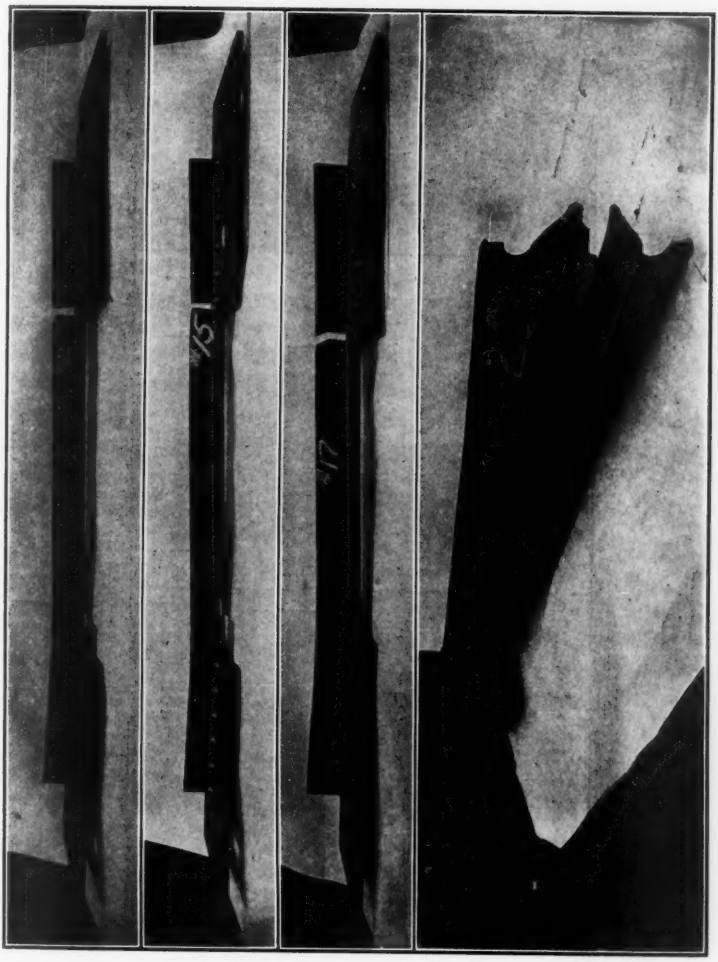

FIG. 5.— VIEWS OF FOUR OF THE TEST SPECIMENS AFTER FRACTURE
From *Engineering Record*

riveted together in pairs, from 46,600 to 52,200 pounds, which is approximately 77 per cent. to 86 per cent. of the strength of the material as developed by the tensile test specimens.

The efficiency of the lug is shown by the fact that for specimens provided with lugs there is an increase over specimens not so provided

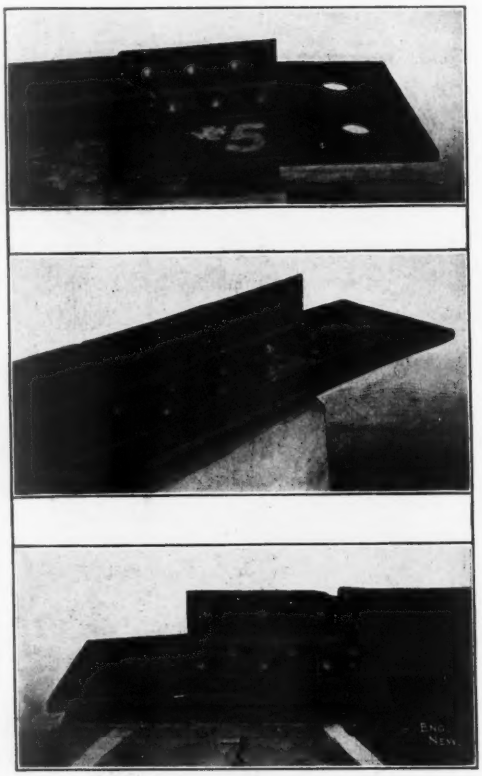

FIG. 6. — NEAR VIEWS OF THREE TYPICAL FRACTURES

of from 4.7 per cent. to 8.7 per cent. in ultimate strength per square inch.

A study of the results of the $4 \times 3 \times \frac{3}{8}$ inch angles without lugs shows that there is a gain of 8 per cent. in the strength per square inch for specimens having the line of pull coinciding with the projection of the centre of gravity line instead of the gauge line for

rivets. It further appears that for these angles the strength per square inch is practically the same for those specimens having the centre of gravity connections *without* lugs as it is for those having the gauge line connections *with* lugs.

TABLE III — SHOWING VALUE OF LUGS

Type.		Ultimate strength per square inch of net section.	Increase in strength per square inch of net area. %
A_1	Without lug	47,400	. .
A_2	With lug	49,600	4.7
B_1	Without lug	40,100	. .
B_2	With lug	43,600	8.7
C_1	Without lug	41,400	. .
C_2	With lug	43,200	4.4
D_1	Without lug	47,400	. .
D_2	With lug	50,600	6.8

Notwithstanding the fact that the net as well as the gross area of the two $3 \times 3 \times \frac{5}{16}$ inch angles is less than in any of the single $6 \times 4 \times \frac{3}{8}$ inch specimens, yet the ultimate load carried by the former is greater in every case.

This is, no doubt, largely due to the greater strength of the material in the double specimens on account of their smaller size and thickness.

In closing, the writer wishes to express his obligations to Messrs. Arthur L. Davis and S. P. Waldron, of the American Bridge Company, for the specimens tested, and to Messrs. A. F. Holmes, instructor, and C. T. Bartlett and H. P. Orcutt, students in the Massachusetts Institute of Technology, who carefully did the work in the laboratory.

BOOK REVIEWS

The Electrical Nature of Matter and Radio-activity[1]

In this work, the author has undertaken the task of presenting in an elementary and nonmathematical form the essential points in the large amount of material published in connection with radio-activity and the electron theory. The book is frankly popular in style, abounding in superlatives and italics, but shows the undoubted interest and enthusiasm of the author in the subject. It furnishes a good survey of the field, and will unquestionably be welcomed by those readers who, as the author says, "have a truly scientific interest in these most recent and important developments in physics and physical chemistry, but to whom a more technical and rigidly mathematical treatment might not appeal."

The greater portion of the book has already appeared in a series of articles in the *Electrical Review*. These articles have been revised, and the whole brought up to date by an additional chapter on recent researches. The first two chapters outline the work of J. J. Thomson on the electrical conductivity of gases, with special reference to the determination of the mass of the cathode particle. A brief presentation of the electron theory of matter follows in the two succeeding chapters. The remaining fourteen chapters are devoted to a discussion of the various radio-active substances, together with the radiations which they emit, the peculiar problems involved in their study, and the disintegration theory of Rutherford.

Such a subject as the electron theory is particularly hard to explain clearly in a nonmathematical form, so that the author is to be pardoned if at times the presentation of this portion seems somewhat unnecessarily detailed for a popular treatise. The book will in some degree meet the needs of all classes of readers except those already conversant with the subject. It should stimulate the general reader to interest in

[1] Harry C. Jones: Electrical Nature of Matter and Radio-activity. New York: Van Nostrand. 1906. $2.00.

these latest fruits of science; and to the scientist who has not investigated this field it will furnish a synopsis of the work hitherto done, together with references to the more important original articles.

C. M. Swan.

A Year-Book of Natural Science[1]

This small volume of 500 pages reviews the progress of science and technology in all their branches for the year 1905–06. When one considers the size of a volume usually required to do this for one branch of science alone, it is evident that the volume under review can accomplish its purpose only in a superficial manner. But from the fact that it is printed in German type it is apparent that this is intended to be only a popular review of the subjects of most interest to the general public.

In physics it takes up the questions of the day, such as the relations between light and electricity, radio-activity, and wireless telegraphy. In other branches of science, however, it may not reflect the most important thought so well; for example, in zoölogy, though the subjects mentioned are interesting, no hint is given of modern work in cytology and its relations to the wider problems which especially occupy the minds of biologists at the present time.

It is a book in which the general reader of scientific tastes would doubtless find much to interest him, and it might serve a teacher of modern languages as a source for sight reading in scientific German.

[1] Jahrbuch der Naturwissenschaften, 1905–06. Edited by Max Wildermann. Freiburg: Herder, 1906.